

UNCLASSIFIED

AD NUMBER
AD809830
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution: Further dissemination only as directed by Nonmetallic Materials Division, Air Force Materials Lab., Attn: Polymer Branch [MANP] Wright-Patterson AFB, OH 45433, Oct 1966; or higher DoD authority.
AUTHORITY
Air Force Materials Lab ltr dtd 7 Dec 1972

THIS PAGE IS UNCLASSIFIED

AFML-TR-66-211

AD0809830

OFFICIAL FILE COPY

**FLUOROAROMATIC CHEMISTRY:
SYNTHESIS OF NITROGEN CONTAINING
FLUOROAROMATIC COMPOUNDS**

*GEORGE BAUM
CHRIST TAMBORSKI*

TECHNICAL REPORT AFML-TR-66-211

OCTOBER 1966

This document may be further distributed by any holder only with specific prior approval of the Polymer Branch (MANP), Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433.

AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

20040225025

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Copies of this report should not be returned to the Research and Technology Division unless return is required by security considerations, contractual obligations, or notice on a specific document.

**FLUOROAROMATIC CHEMISTRY:
SYNTHESIS OF NITROGEN CONTAINING
FLUOROAROMATIC COMPOUNDS**

*GEORGE BAUM
CHRIST TAMBORSKI*

This document may be further distributed by any holder only with specific prior approval of the Polymer Branch (MANP), Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433.

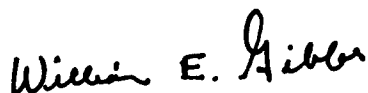
FOREWORD

This report was prepared by the Polymer Branch of the Nonmetallic Materials Division. The work was conducted under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." It was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. Dr. George Baum served as Project Engineer.

This report covers research conducted from January 1963 to January 1965. The manuscript was released by the author in November 1965 for publication as an RTD technical report.

The author is indebted to the Analytical Branch, Materials Physics Division, and its contractors for elemental analyses, nuclear magnetic resonance studies, and thermal stability determinations. The F^{19} n.m.r. spectra were interpreted by John Pustinger, Jr., and J. E. Strobel of the Monsanto Research Corporation, Dayton, Ohio.

This technical report has been reviewed and is approved.



WILLIAM E. GIBBS
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

The present research was undertaken as part of a broad program to investigate the potential utility of polyfluoroaromatic compounds as thermally or oxidatively resistant nonmetallic materials. Nucleophilic substitution reactions of polyfluoroanilines with fluoroaromatics led to a variety of polyfluorodiphenylamines which are structurally related to known antioxidants. These amines were further converted into diamines and diacids. Several model compounds were prepared for thermal stability studies. Amides of secondary polyfluoroamines appear to possess a high degree of stability.

TABLE OF CONTENTS

	PAGE
INTRODUCTION	1
DISCUSSION	2
General Preparation of Polyfluorodiphenylamines	2
Preparation of Difunctional Polyfluorodiphenylamines	2
Preparation of Model Compounds for Thermal Stability Determinations	4
EXPERIMENTAL	8
Decafluorodiphenylamine (I)	8
4H-Nonafluorodiphenylamine (II)	8
4-Bromo-nonafluorodiphenylamine (III)	8
4H,4'-Bromo-octafluorodiphenylamine (IV)	9
Di(4H-tetrafluorophenyl)amine (V)	9
N-Pentafluorophenyl-2-heptafluoronaphthylamine (VI)	9
N-Methyl-N-pentafluorophenyl-2-heptafluoronaphthylamine (VII)	9
N-Methyldecafluorodiphenylamine (VIII)	9
Di(4H-tetrafluorophenyl)acetamide (IX)	10
Decafluorodiphenylacetamide (X)	10
Pentadecafluorodiphenylbenzamide (XI)	10
1,2-Di(pentafluorobenzoyl)hydrazine (XII)	10
2,5-Di(pentafluorophenyl)-1,3,4-oxadiazole (XIII)	11
Decafluorobenzanilide (XIV)	11
Di(4-hydrazinotetrafluorophenyl)acetamide (XV)	11
Di(4-acetophenone hydrazonetetrafluorophenyl)acetamide (XVa)	11
Di(4-aminotetrafluorophenyl)acetamide (XVI)	11
Metallation and Carbonation of Di(4H-tetrafluorophenyl)amine	12
Reaction of Di(4-carboxytetrafluorophenyl)amine with Diazomethane	12

TABLE OF CONTENTS (Cont'd)

	PAGE
Reaction of 4H,4'-carboxyoctafluorodiphenylamine with Diazomethane	13
N,N,N',N'-Tetraphenyl-1,4-tetrafluorophenylenediamine (XXIV)	13
REFERENCES	14
SPECTRA	15

SPECTRA

COMPOUND NO.		PAGE
I.	Decafluorodiphenylamine	15
II.	4H-Nonafluorodiphenylamine	16
III.	4-Bromo-nonafluorodiphenylamine	17
IV.	4H,4'-Bromo-octafluorodiphenylamine	18
V.	Di(4H-tetrafluorophenyl)amine	19
VI.	N-Pentafluorophenyl-2-heptafluoronaphthylamine	20
VII.	N-Methyl-N-pentafluorophenyl-2-heptafluoronaphthylamine	21
VIII.	N-Methyldecafluorodiphenylamine	22
IX.	Di(4-H-tetrafluorophenyl)acetamide	23
X.	Decafluorodiphenylacetamide	24
XI.	Pentadecafluorodiphenylbenzamide	25
XII.	1,2-Di(pentafluorobenzoyl)hydrazine	26
XIII.	2,5-Di(pentafluorophenyl)-1,3,4-oxadiazole	27
XIV.	Decafluorobenzanilide	28
XV.	Di(4-hydrazinotetrafluorophenyl)acetamide	29
XVI.	Di(4-aminotetrafluorophenyl)acetamide	30
XVII.	Di(4-carboxytetrafluorophenyl)amine	31
XVIII.	4H-4'-Carboxyoctafluorodiphenylamine	32
XIX.	Di(4-carbomethoxytetrafluorophenyl)amine	33
XX.	N-Methyl-di(4-carbomethoxytetrafluorophenyl)amine	34
XXI.	4H,4'-Carbomethoxyoctafluorodiphenylamine	35
XXII.	N-Methyl-4H,4'-carbomethoxyoctafluorodiphenylamine	36

INTRODUCTION

A broad investigation into the chemistry of fluoroaromatic compounds was initiated several years ago as a part of a continuing program to uncover and develop novel classes of thermally stable materials. Interest in fluoroaromatic chemistry was stimulated by several factors. The initial report of the preparation of hexafluorobenzene suggested that the material was extremely thermally stable (Reference 1). Subsequent measurements of the stability of hexafluorobenzene by the isoteniscope method assigned a "decomposition temperature" of at least 650°C; under comparable conditions, benzene has a "decomposition temperature" of 600°C (Reference 2). Few laboratories were engaged in a study of fluoroaromatic chemistry, largely a result of the unavailability of hexafluorobenzene. When hexafluorobenzene became available in research quantities, an opportunity developed to explore the possibility of preparing heat-stable organic materials based on fluoroaromatic chemistry.

The present report deals with the preparation and reactions of a variety of fluoroaromatic amines. The objective of this research was the synthesis of fluorinated analogs of known aromatic amine antioxidants, difunctional monomers, and model compounds for thermal stability determinations.

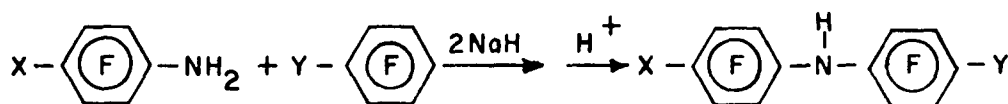
DISCUSSION

GENERAL PREPARATION OF POLYFLUORODIPHENYLAMINES

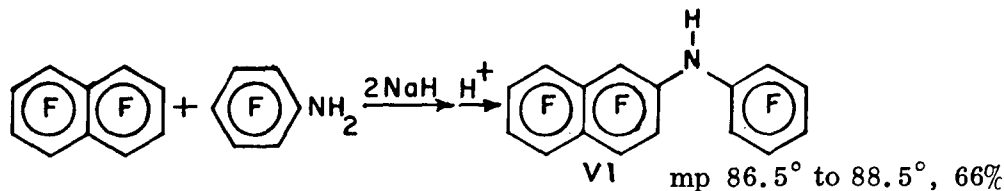
When this work was initiated, good synthetic routes to polyfluorodiphenylamines were not available. Decafluorodiphenylamine had been obtained as a minor product from the reaction of hexafluorobenzene with sodamide (Reference 3). Di(4-methoxytetrafluorophenyl)amine was observed to be a minor product (Reference 4) from the reaction of pentafluoroanisole with sodamide.

A direct route for the preparation of decafluorodiphenylamine was realized from the reaction of pentafluoroaniline and hexafluorobenzene in the presence of two equivalents of sodium hydride. The reaction involves nucleophilic substitution of a fluoroaromatic substrate by the anion (mono or di) of pentafluoroaniline. Two equivalents of sodium hydride are required as the product before hydrolysis is the sodium salt of decafluorodiphenylamine. It is not clear at what stage of the reaction the second hydrogen is lost. The amines prepared by this reaction are reported in Table I.

TABLE I
POLYFLUORODIARYLAMINES



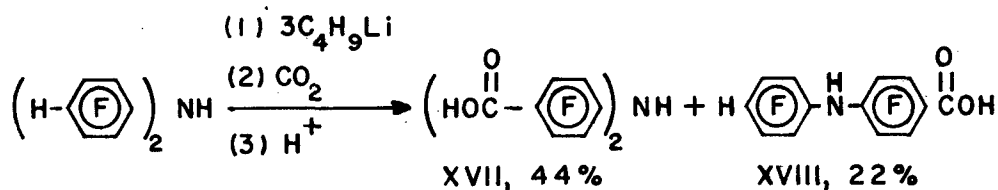
	X	Y	mp	% Yield
I	F	F	85.5-86	64
II	H	F	84-85	49
		H	85.5-86.5	39
III	F	Br	105.5-107.5	36
IV	H	Br	118-120	46
V	H	H	126.5-127.5	27



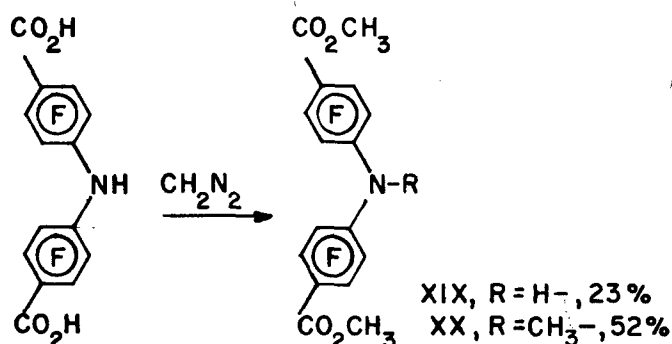
PREPARATION OF DIFUNCTIONAL POLYFLUORODIPHENYLAMINES

Current in-house research has led to convenient preparative methods for the formation of polyfluoroaromatic acids (Reference 5) and primary amines (Reference 6). Application of these reactions to the polyfluorodiarylamines would provide polyfunctional intermediates which are required for the preparation of a wide variety of fluoroaromatic polymers.

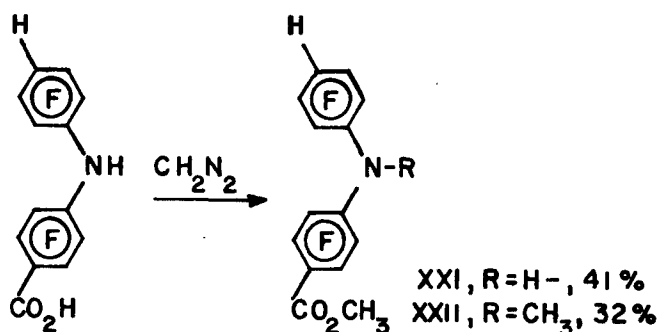
Thus, di(4H-tetrafluorophenyl)amine upon reaction with three equivalents of butyllithium followed by carbonation and acidification gives di(4-carboxytetrafluorophenyl)amine (XVII), mp 299° to 302° in 44-percent yield. The diacid XVII is accompanied by 22 percent of 4H,4'-carboxy-octafluorodiphenylamine (XVIII), mp 200° to 201.5°.



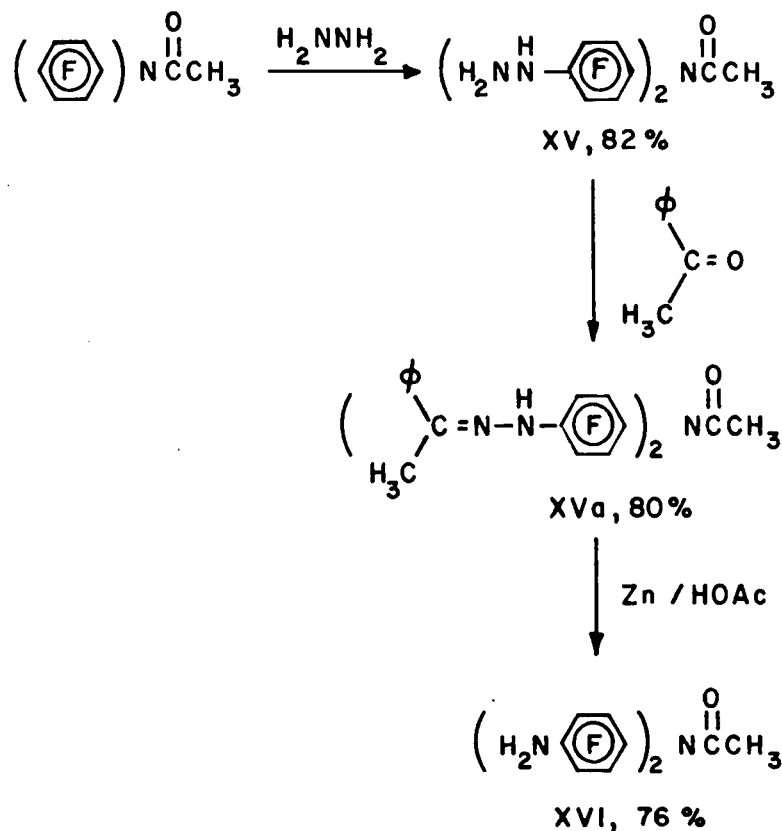
Methylation of the acids by diazomethane results in concomitant methylation of the N-H group. From acid XVII, N-methyl-di(4-carbomethoxytetrafluorophenyl)amine (XX), mp 101° to 102.5°, and di(4-carbomethoxytetrafluorophenyl)amine (XIX), mp 140° to 142°, are produced.



Nitrogen methylation was also observed upon reaction of diazomethane with 4H,4'-carboxy-di(tetrafluorophenyl)amine; N-methyl-4H,4'-carbomethoxy-di(tetrafluorophenyl)amine (XXII), mp 68° to 69°, and 4H,4'-carbomethoxy-di(tetrafluorophenyl)amine (XXI), mp 100° to 104°, are obtained.



Di(4-aminotetrafluorophenyl)acetamide (XVI), mp 201° to 203°, is obtained by a series of reactions starting with the formation of di(4-hydrazinotetrafluorophenyl)acetamide (XV), mp 153° to 155°, conversion to the dihydrazone (XVa) with acetophenone and reduction with zinc in acetic acid.

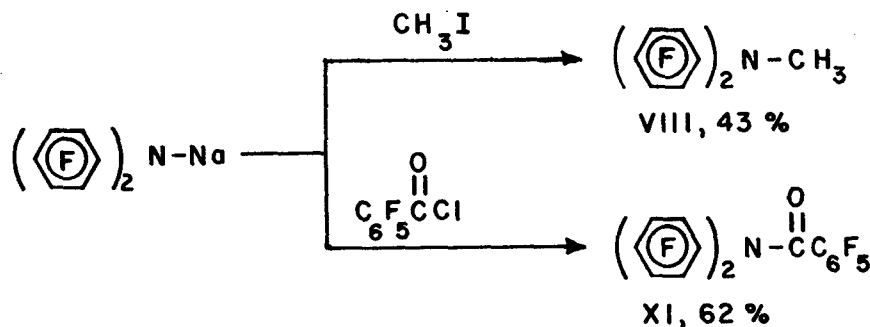


PREPARATION OF MODEL COMPOUNDS FOR THERMAL STABILITY DETERMINATIONS

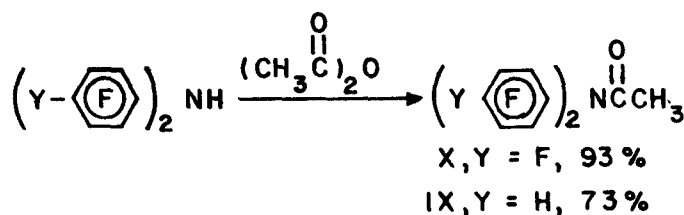
Early attempts to prepare a useful heat-stable fluoroaromatic fluid involved the preparation of poly(perfluorophenyl)ether. The results of this program were disappointing in that it was found that decafluorodiphenyl ether possessed an isoteniscope decomposition temperature of 377° compared to 454° for the hydrogenic analog (Reference 7).

It was of interest to determine if nitrogen-linked fluoroaromatic compounds offered an advantage with respect to thermal stability. Accordingly the preparation of a number of model compounds was undertaken.

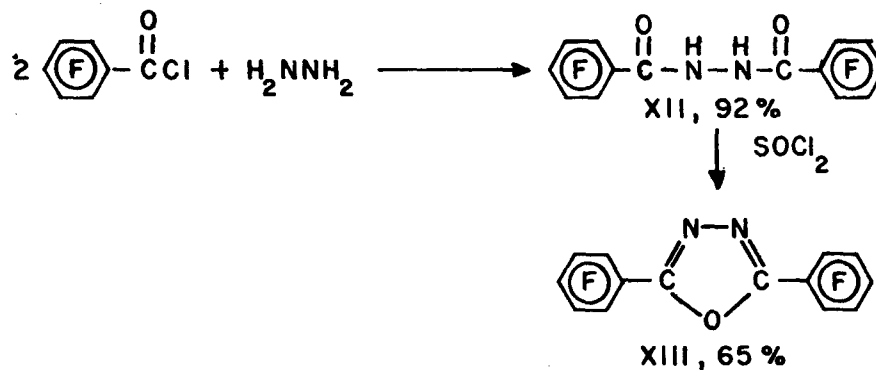
Pentafluoroaniline reacts readily with pentafluorobenzoyl chloride to give decafluorobenzanilide (XIV), mp 181° to 181.5°, 61.5 percent. Decafluorodiphenylamine reacts vigorously with sodium hydride to form N-sodiodecafluorodiphenylamine. The sodium salt undergoes normal reaction with methyl iodide and pentafluorobenzoyl chloride to yield N-methyldecafluorodiphenylamine (VIII), mp 64°, and pentadecafluorodiphenylbenzamide (XI), mp 126°, respectively.



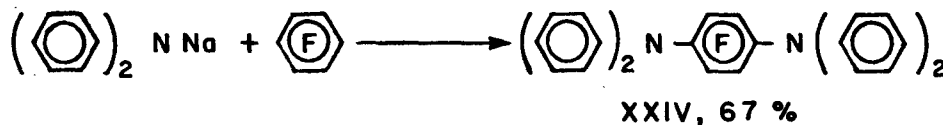
The reaction of acetic anhydride with decafluorodiphenylamine and di(4H-tetrafluorophenyl)-amine gives decafluorodiphenylacetamide (X), mp 124°, and di(4H-tetrafluorophenyl)acetamide (IX), mp 112°, respectively.



Pentafluorobenzoyl chloride reacts with hydrazine to produce 1,2-di(pentafluorobenzoyl)-hydrazine (XII), mp 258° to 260°. Cyclodehydration of the hydrazide with thionyl chloride results in 2,5-di(pentafluorophenyl)-1,3,4-oxadiazole (XIII), mp 156.5° to 157.5°.



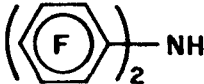
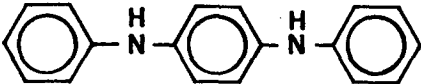
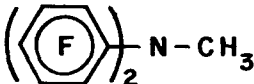
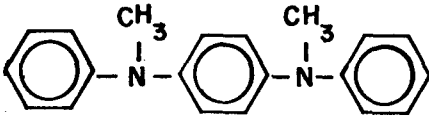
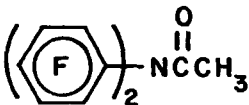
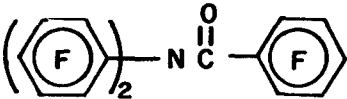
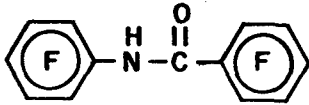
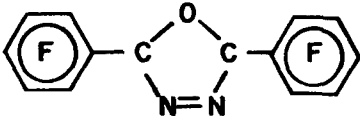

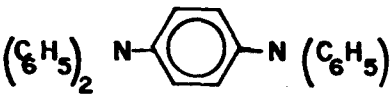
The sodium salt of diphenylamine reacts with hexafluorobenzene to give N,N,N',N'-tetraphenyl-1,4-tetrafluorophenylenediamine (XXIV), mp 198° to 199°.



The relative thermal stabilities of the model compounds were determined by the isoteniscope method. The decomposition temperature is defined as the temperature at which the rate of volatile product formation corresponds to one mole percent per hour. In Table II the decomposition temperatures of the fluoroaromatic compounds are presented along with related hydrogenic analogs.

From Table II, it is apparent that certain structural units should be avoided. However, the pentadecafluorodiphenylbenzamide is of sufficient stability to warrant further investigation into the preparation of functional fluoroarylamides and related polymers.

TABLE II
RELATIVE THERMAL STABILITIES OF
MODEL FLUOROAROMATIC COMPOUNDS (REFERENCE 9)

	T_D °C
	357
	ca 265 (Reference 10)
	ca 282
	338 (Reference 10)
	Less than 316
	ca 427
	ca 160
	ca 288
	449
	405 (Reference 10)

EXPERIMENTAL

Decafluorodiphenylamine (I). - A solution of pentafluoroaniline (36.6 grams, 0.20 mole) in 100 ml of ether was added dropwise to a mixture of hexafluorobenzene (105.6 grams, 0.60 mole) and sodium hydride (19.2 grams, 0.40 mole, 50-percent dispersion in mineral oil) in 50 ml of ether at reflux. The reaction mixture became dark green as the addition proceeded. The reaction was refluxed for 10 hours, cooled, poured into 200 ml of ice water, acidified with conc. HCl and extracted with ether. The ether extract was dried over magnesium sulfate, evaporated to dryness, and the residue was sublimed (60°/11 mm) to give 40.39 grams of the desired product, mp 80° to 83°. The purple waxy residue was steam distilled to give an additional 4.42 grams (64% combined yield) of product. Resublimation afforded the analytical sample, mp 85.5° to 86°.

The F^{19} n.m.r. spectra in benzene exhibited multiplets centered at 76.3 and 85.6 ppm from trifluoroacetic acid. The area ratios were 4:6 respectively.

Anal. Calcd. for $C_{12}HF_{10}N$: C, 41.28; H, 0.27; F, 54.42; N, 4.01; mol.wt, 313.

Found: C, 41.07; H, 0.57; F, 54.16; N, 4.22; mol.wt, 358.

4H-Nonafluorodiphenylamine (II). - A. The addition of 4H-tetrafluoroaniline (8.40 grams, 0.05 mole) to hexafluorobenzene (8.80 grams, 0.05 mole) and sodium hydride (4.80 grams, 0.10 mole, 50% dispersion in mineral oil) in ether gave 8.16 grams (49%) of the desired product. Recrystallization from ligroin, bp 38° to 50°, gave the analytical sample, mp 81.5° to 82.5°.

The F^{19} n.m.r. spectra in benzene exhibited multiplets centered at 61.3, 74.6, 77.8, and 84.2 ppm from trifluoroacetic acid.

Anal. Calcd. for $C_{12}H_2F_9N$: C, 43.52; H, 0.61; F, 51.64; N, 4.23; mol.wt, 331.

Found: C, 43.39; H, 0.79; F, 51.83; N, 3.99; mol.wt, 342.

B. The addition of pentafluoroaniline (9.15 grams, 0.05 mole) in ether (40 ml) to pentafluorobenzene (8.40 grams, 0.05 mole) and sodium hydride (5.2 grams, 0.11 mole, 50% dispersion) in mineral oil in ether (10 ml) at reflux gave, upon work-up, the desired product 6.50 grams, (39%) as pale pink needles, mp 85.5° to 86.5° (after sublimation 90°/1 mm). The n.m.r. and infrared spectrum of the sample were identical to the product from reaction A above.

4-Bromo-nonafluorodiphenylamine (III). - The addition of pentafluoroaniline (9.15 grams, 0.05 mole) to pentafluorobromobenzene (12.35 grams, 0.05 mole) and sodium hydride (2.62 grams, 0.55 mole, 50% dispersion in mineral oil) in THF gave 6.06 grams (36%) of the desired product. Two recrystallizations from ligroin bp 60° to 90° gave the analytical sample, mp 105.5° to 107.5°.

The F^{19} n.m.r. spectra in benzene exhibited multiplets centered at 58.8, 75.6, 77.8, 85.0, and 86.8 ppm from trifluoroacetic acid.

Anal. Calcd. for $C_{12}HBrF_9N$: C, 35.15; H, 0.05; F, 41.71; N, 3.41; mol.wt, 410.

Found: C, 34.95; H, 0.32; F, 40.93; N, 3.18; mol.wt, 407.

4H,4'-Bromo-octafluorodiphenylamine (IV). - The addition of 4H-tetrafluoroaniline (25.20 grams, 0.15 mole) in THF (50 ml) to a mixture of bromopentafluoroaniline (37.10 grams, 0.15 mole) and sodium hydride (55% dispersion in mineral oil, 13.10 grams, 0.30 mole) in refluxing THF (150 ml) produced the desired product (24.62 grams, 46%) as white crystals mp 118° to 120° (from ligroin, bp 60° to 90°).

The F^{19} n.m.r. spectra in benzene exhibited three multiplets centered at 57.2, 75.7, and 62.3 ppm.

Anal. Calcd. for $C_{12}H_2BrF_8N$: C, 36.76; H, 0.52; Br, 20.38; F, 38.77; N, 3.57; mol.wt, 392.

Found: C, 36.71; H, 0.64; Br, 20.17; F, 38.80; N, 3.51; mol.wt, 379.

Di(4H-tetrafluorophenyl)amine (V). - The addition of 4H-tetrafluoroaniline (41.00 grams, 0.25 mole) to pentafluorobenzene (39.25 grams, 0.25 mole) and sodium hydride (24 grams, 0.50 mole, 50% dispersion in mineral oil) in ether gave 40.4 grams (52%) of the desired product. Recrystallization from ligroin, bp 60° to 90°, gave the analytical sample as white plates, mp 126.5° to 127.5°.

The F^{19} n.m.r. spectra in benzene exhibited multiplets centered at 61.0 and 75.8 ppm from trifluoroacetic acid.

Anal. Calcd. for $C_{12}H_3F_8N$: C, 46.02; H, 0.96; F, 48.54; N, 4.47; mol.wt, 313.

Found: C, 46.34; H, 1.07; F, 49.47; N, 4.36; mol.wt, 315.

N-Pentafluorophenyl-2-heptafluoronaphthylamine (VI). - The addition of pentafluoroaniline (4.5 grams, 0.025 mole) to octafluoronaphthalene (7.75 grams, 0.025 mole) and sodium hydride (2.64 grams, 0.055 mole, 50% dispersion in mineral oil) in THF gave 7.13 grams (65.5%) of the desired product. Two recrystallizations from ligroin bp 60° to 90° gave the analytical sample, mp 86.5° to 88.5°.

The F^{19} n.m.r. spectra in benzene was consistent for a 2-substituted naphthalene.

Anal. Calcd. for $C_{16}HF_{12}N$: C, 44.16; H, 0.23; N, 3.22; F, 52.39.

Found: C, 44.91; H, 0.50; N, 3.32; F, 53.90.

N-Methyl-N-pentafluorophenyl-2-heptafluoronaphthylamine (VII). - A 5-ml aliquot of the reaction mixture resulting from the addition of pentafluoroaniline to octafluoronaphthalene and two equivalents of sodium hydride in THF was treated with 1.0 grams of iodomethane. After work-up, there was obtained a small amount of material which was recrystallized from ligroin, bp 38° to 50°, to give the desired product, mp 84.5° to 84.6°. The infrared and F^{19} n.m.r. absorption spectra are consistent with the proposed structure.

N-Methyldecafluorodiphenylamine (VIII). - A solution of iodomethane (1.42 grams, 0.01 mole) in 5 ml of THF was added at room temperature to a solution of N-sodiodecafluorodiphenylamine prepared from decafluorodiphenylamine (3.39 grams, 0.01 mole) and sodium hydride (0.50

grams, 0.011 mole, 50% dispersion in mineral oil) in 15 ml of THF. The reaction was stirred for 2 hours at room temperature and then poured into 100 ml 5-percent Na_2CO_3 solution. The THF layer was phase separated, dried over sodium sulfate, evaporated to dryness, and the residue recrystallized from cyclohexane to give 1.68 grams of the desired product, mp 60° to 63° . The filtrate was shown by VPC to contain an additional 0.95 gram of product thus giving a total yield of 74 percent. Two recrystallizations from cyclohexane gave the analytical sample, mp 63.5° to 64° .

Anal. Calcd. for $\text{C}_{13}\text{H}_3\text{F}_{10}\text{N}$: C, 42.99; H, 0.83; F, 52.32; N, 3.86; mol.wt, 363.

Found: C, 42.85; H, 0.87; F, 51.79; N, 4.03; mol.wt, 386.

Di(4H-tetrafluorophenyl)acetamide (IX). - Treatment of 4,4'-dihydrooctafluorodiphenylamine (15 grams, 0.0479 mole) with acetic anhydride gave 13.29 grams (73%) of the desired product as white prisms, mp 111° to 112° .

Anal. Calcd. for $\text{C}_{14}\text{H}_5\text{F}_8\text{NO}$: C, 47.34; H, 1.42; N, 3.94.

Found: C, 47.57; H, 1.61; N, 3.93.

Decafluorodiphenylacetamide (X). - A solution of decafluorodiphenylamine (16.95 grams, 0.0485 mole) in 25 ml of glacial acetic acid containing several drops of conc. H_2SO_4 was refluxed for 17.5 hours. The reaction was then poured into 200 ml of ice water and the white precipitate was collected by filtration, dried and recrystallized from benzene to give 17.68 grams (93%) of the desired product as white prisms, mp 122.5° to 124° .

Anal. Calcd. for $\text{C}_{14}\text{H}_3\text{F}_{10}\text{NO}$: C, 42.98; H, 0.77; N, 3.58.

Found: C, 43.18; H, 1.06; N, 3.67.

Pentadecafluorodiphenylbenzamide (XI). - A solution of pentafluorobenzoyl chloride (4.62 grams, 0.020 mole) in 20 ml of THF was added dropwise at room temperature to a solution of N-sodiodecafluorodiphenylamine prepared from sodium hydride (1.00 gram, 0.021 mole, 50% dispersion in mineral oil) and decafluorodiphenylamine (6.78 grams, 0.020 mole) in 50 ml of THF. The reaction was refluxed for 3 hours, cooled, and poured into 200 ml of a 5-percent Na_2CO_3 solution. The THF layer was phase separated, dried over magnesium sulfate, and evaporated to dryness. The residue was recrystallized from ligroin, bp 60° to 90° , to give 7.31 grams (62.5%) of the desired product, mp 120° to 123° . A second recrystallization from the same solvent gave the analytical sample, mp 125.5° to 126° .

Anal. Calcd. for $\text{C}_{19}\text{F}_{15}\text{NO}$: C, 42.01; H, 0.00; F, 52.47; N, 2.58; mol.wt, 543.

Found: C, 42.15; H, --; F, 51.24; N, 2.49; mol.wt, 539.

1,2-Di(pentafluorobenzoyl)hydrazine (XII). - A solution of pentafluorobenzoyl chloride (25.2 grams, 0.109 mole) in 50 ml of DMF was added dropwise to an ice-cooled bath solution of 95 + percent hydrazine (1.60 grams, 0.05 mole) and triethylamine (10.1 grams, 0.10 mole) in 50 ml of DMF. After addition was complete the reaction mixture was heated on a steam bath for 0.5 hour, cooled and poured into 500 ml of water. The precipitate was filtered, washed with water, and recrystallized from 95-percent ethanol to give 19.37 grams (92.3%) of crude product, mp 220° to 260° . Recrystallization from 95-percent ethanol gave the analytical sample, mp 258° to 260° .

Anal. Calcd. for $C_{14}H_2F_{10}N_2O_2$: C, 40.02; H, 0.48; F, 45.22; N, 6.67.

Found: C, 40.40; H, 0.3; F, 44.9; N, 6.94.

2,5-Di(pentafluorophenyl)-1,3,4-oxadiazole (XIII). - A solution of 1,2-di(pentafluorobenzoyl)hydrazine (2.00 grams, 0.00476 mole) in 40 ml of thionyl chloride was refluxed for 21 hours. The thionyl chloride was stripped off and the residue was poured into 100 ml of ice water. The organic material was extracted with ether which was dried over magnesium sulfate and evaporated to dryness to give 1.24 grams (65%) of crude product, mp 155° to 160° . Recrystallization from methanol gave the analytical sample as pale yellow needles, mp 156.5° to 157.5° .

Anal. Calcd. for $C_{14}F_{10}N_2O$: C, 41.81; F, 47.25; N, 6.96; mol.wt, 402.

Found: C, 41.53; F, 46.2; N, 7.07; mol.wt, 403.

Decafluorobenzanilide (XIV). - To a hot stirred solution of pentafluorobenzoyl chloride (6.94 grams, 0.302 mole) in 10 ml of benzene, a solution of pentafluoroaniline (5.06 grams, 0.027 mole) in 5 ml of benzene was added dropwise. The reaction was refluxed for one hour, cooled, and filtered to give 6.43 grams (61.5%) of crude product, mp 179° to 184° . Recrystallization from benzene gave the analytical sample as white needles, mp 181° to 181.5° .

Anal. Calcd. for $C_{13}HF_{10}NO$: C, 41.40; H, 0.27; F, 50.38; N, 4.20; mol.wt, 377.

Found: C, 41.88; H, 0.23; F, 49.23; N, 4.18; mol.wt, 364.

Di(4-hydrazinotetrafluorophenyl)acetamide (XV). - A solution of di(pentafluorophenyl)acetamide (11.43 grams, 0.03 mole) and hydrazine (95+%, 4.04 grams, 0.12 mole) in dioxane (80 ml) was stirred at room temperature for 18 hours. The solution gradually became cloudy and a white precipitate separated from solution. The reaction mixture was poured into water (200 ml) and extracted with ether. The yellow viscous oil remaining after evaporation of the ether was recrystallized twice from benzene to give the desired product (10.20 grams, 81.9%) as white crystals, mp 153° to 155° .

Anal. Calcd. for $C_{14}H_9F_8N_5O$: C, 40.49; H, 2.18; F, 16.86.

Found: C, 40.77; H, 2.16; F, 16.81.

Di(4-acetophenone hydrazone tetrafluorophenyl)acetamide (XVa). - A solution of di(4-hydrazinotetrafluorophenyl)acetamide (4.50 grams, 0.0108 mole) and acetophenone (1.30 grams, 0.108 mole) in 95-percent ethanol (50 ml) containing one ml acetic acid was refluxed for two hours. The reaction mixture was poured into water (200 ml) and filtered to give the desired product (5.39 grams, 80.5%) as white crystals, mp 201° to 203° , after two recrystallizations from benzene.

The F^{19} n.m.r. spectra in benzene displayed a doublet centered at 85 ppm and a singlet at 72.5 ppm.

Anal. Calcd. for $C_{14}H_7F_8N_3O$: C, 43.65; H, 1.83; N, 10.90.

Found: C, 44.49; H, 1.87; N, 10.54.

Di(4-aminotetrafluorophenyl)acetamide (XVI). - A solution of the hydrazone XVa (5.05 grams, 0.00815 mole) in glacial acetic acid (100 ml) containing zinc dust (10 grams) was refluxed for one hour and filtered hot. The filtrate was poured into ice water (30 ml), cooled, and filtered

to give the desired product (2.39 grams, 76%) as white crystals mp 201° to 203° after two recrystallizations from benzene-ligroin (bp 60° to 90°).

The F^{19} n.m.r. spectra in benzene exhibited three sets of multiplets centered at 87.4 ppm, 82.3 ppm, and 72.5 ppm from trifluoroacetic acid. An unusual field effect was observed with polyfluorodiphenylacetamides resulting in nonequivalence of the meta fluorines.

Anal. Calcd. for $C_{14}H_7F_8N_3O$: C, 43.65; H, 1.83; F, 10.90.

Found: C, 44.49; H, 1.87; F, 10.52.

Metallation and Carbonation of Di(4H-tetrafluorophenyl)amine. - Butyllithium (222 ml of a hexane solution, 0.255 mole) was added, with stirring to a solution of di(4H-tetrafluorophenyl)-amine (26.19 grams, 0.0836) in 250 ml of ether at -75°. The addition was complete in 1.25 hours and 150 ml of ether was added. Gilman color test IIA was negative within 0.5 hour after addition was complete. The reaction mixture was carbonated and worked-up as previously reported. The residue remaining after ether was removed was stirred with hot toluene and filtered to give 14.74 grams (44%) of di(4-carboxytetrafluorophenyl)amine (XVII), mp 299° to 302°.

The F^{19} n.m.r. spectra in acetone exhibited multiplets at 62.5 and 74.8 ppm.

Anal. Calcd. for $C_{14}H_3F_8NO_4$: C, 41.91; H, 0.75; N, 3.49; M.W., 401; Neut. Eq., 200.

Found: C, 42.40; H, 1.02; N, 3.53; M.W., 377; Neut. Eq., 224.

The toluene filtrate was chilled and filtered to give 3.70 grams of 4H-4'-carboxyoctafluorodiphenylamine (XVIII), mp 190° to 200°. The toluene solution was evaporated to dryness and the residue boiled in ligroin, bp 90° to 120°, to give an additional 2.75 grams of the mono acid (22.5%). Recrystallization from water-methanol provided the analytical sample, mp 200° to 201.5°.

The F^{19} n.m.r. spectra in acetone exhibited multiplets at 63.3, 73.9, and 77.5 ppm.

Anal. Calcd. for $C_{13}H_3F_8NO_2$: C, 43.75; H, 0.85; N, 3.92; M.W., 357; Neut. Eq., 343.

Found: C, 43.76; H, 1.26; N, 4.01; M.W., 345; Neut. Eq., 360.

Reaction of Di(4-carboxytetrafluorophenyl)amine with Diazomethane. - To an ice-cooled bath solution of di(4-carboxytetrafluorophenyl)amine (12.03 grams, 0.03 mole) in 150 ml of ether, diazomethane in ether was added until no further gas evolution occurred. The yellow solution was stirred for 2 hours at room temperature and then poured into 3-percent acetic acid. The ethereal layer was dried over magnesium sulfate, evaporated to dryness, and the residue recrystallized from ligroin, bp 90° to 120°, to give 2.92 grams (23%) of di(4-carbomethoxytetrafluorophenyl)amine (XIX), mp 140° to 142°.

The F^{19} n.m.r. spectra in benzene exhibited multiplets at 61.9 and 75.5 ppm.

The ligroin filtrate yielded 6.86 grams (52%) of N-methyl-di(4-carbomethoxytetrafluorophenyl)amine (XX), mp 101° to 102.5°.

Anal. Calcd. for $C_{17}H_9F_8NO_4$: C, 46.06; H, 2.05; N, 3.16.

Found: C, 46.24; H, 2.22; N, 3.37.

Reaction of 4H,4'-carboxyoctafluorodiphenylamine with Diazomethane. - To a solution of 4H,4'-carboxyoctafluorodiphenylamine (3.43 grams, 0.01 mole) in 50 ml of ether, diazomethane in ether was added until no further gas evolution occurred. The yellow solution was stirred overnight, evaporated to dryness, and the residue recrystallized from ligroin, bp 90° to 120°, to give 1.52 grams (41%) of 4H,4'-carbomethoxyoctafluorodiphenylamine (XXI) mp 100° to 104°. A second recrystallization from the same solvent afforded the analytical sample.

Anal. Calcd. for $C_{15}H_5F_8NO_2$: C, 45.30; H, 1.36; F, 40.95; N, 3.77; mol.wt, 371.

Found: C, 45.88; H, 1.56; F, 41.57; N, 3.81; mol. wt, 368.

The ligroin filtrate yielded 1.23 grams (32%) of N-methyl-4H,4'-carbomethoxyoctafluorodiphenylamine (XXII), mp 68° to 69°, purified by sublimation, 85°/1 mm.

Anal. Calcd. for $C_{14}H_7F_8NO_2$: C, 46.77; H, 1.83; N, 3.63; mol.wt, 385.

Found: C, 45.81; H, 1.81; N, 3.70; mol.wt, 408.

N,N,N',N'-Tetraphenyl-1,4-tetrafluorophenylenediamine (XXIV). - A solution of hexafluorobenzene (9.50 grams, 0.05 mole) in 50 ml of THF was added dropwise to a refluxing solution of N-sodiodiphenylamine prepared from diphenylamine (16.92 grams, 0.10 mole) and sodium hydride (2.3 grams, 0.10 mole, 50% dispersion in mineral oil). The reaction was refluxed for 3 hours, cooled and poured into 200 ml of 5-percent Na_2CO_3 solution. The THF layer was phase separated, dried over magnesium sulfate, evaporated to dryness and the residue was recrystallized from benzene to give 7.31 grams (62.5%) of the desired product. Recrystallization from benzene gave the analytical sample, mp 198° to 199° (Reference 8, mp 198° to 200°).

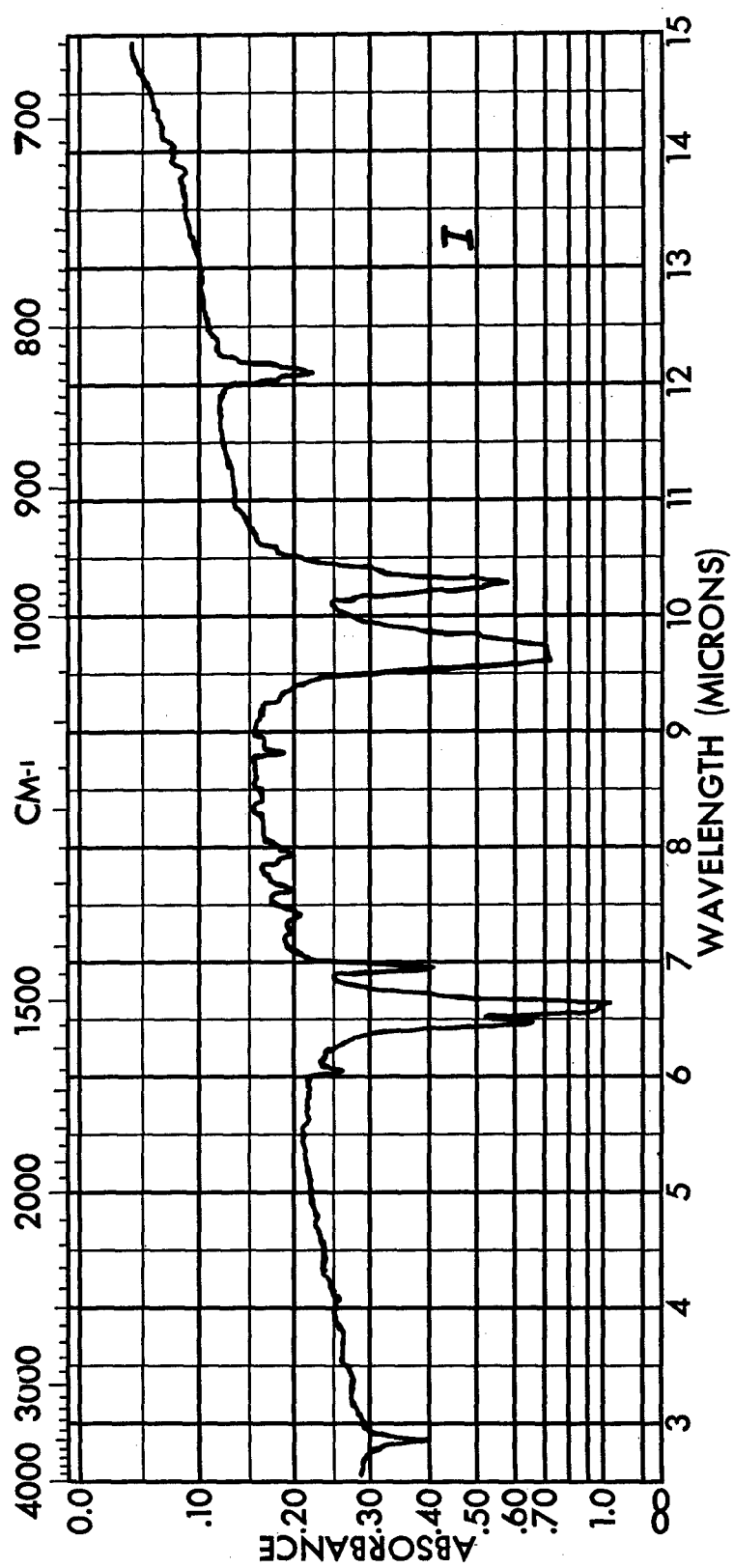
The F^{19} n.m.r. spectra in benzene exhibited a single band at 65.0 ppm from trifluoroacetic acid.

Anal. Calcd. for $C_{30}H_{20}F_4N_2$: C, 74.37; H, 4.16; F, 15.69; N, 5.80; mol.wt, 484.

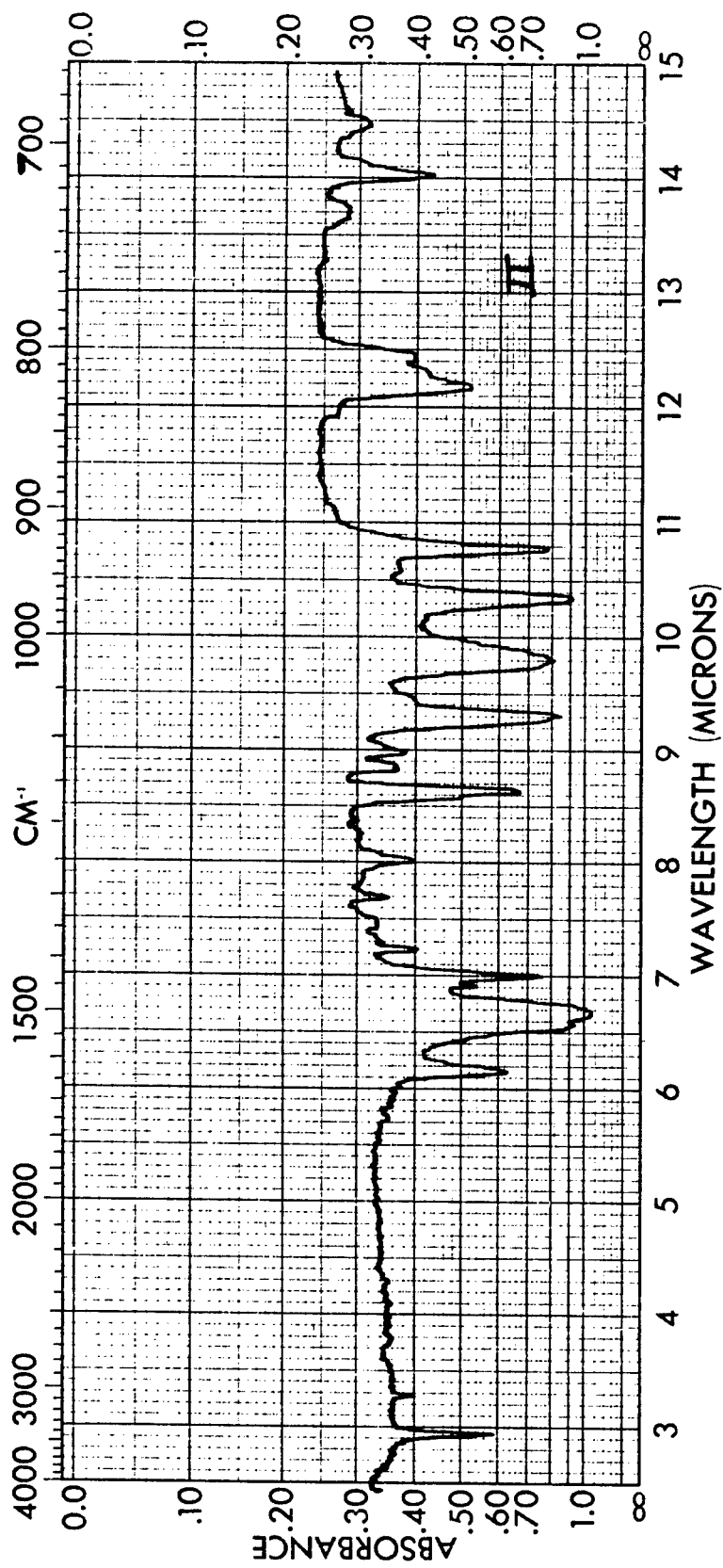
Found: C, 73.50; H, 3.92; F, 15.84; N, 6.28; mol.wt, 495.

REFERENCES

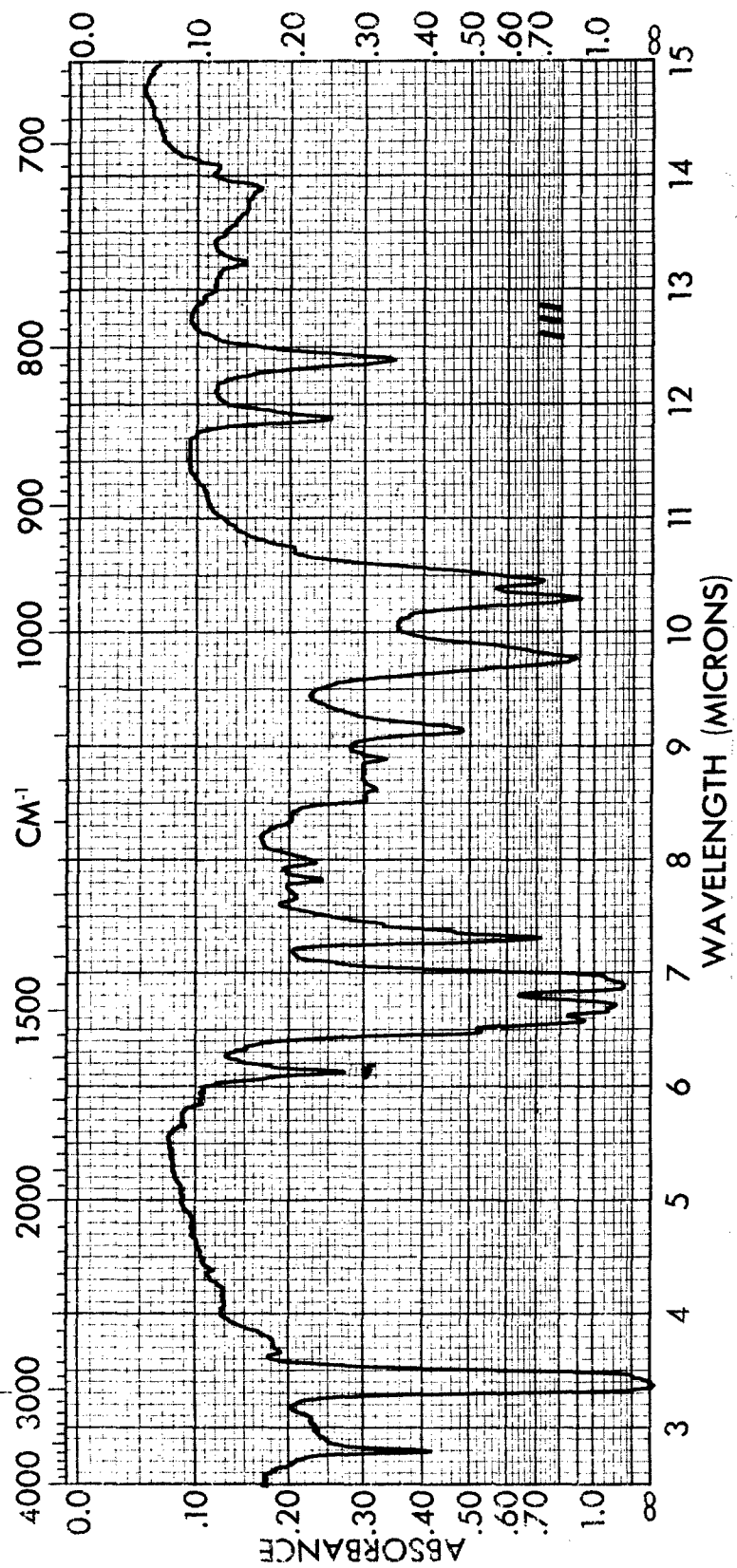
1. Y. Desirant, Bull. Acad. Roy. Belg. Classe. Sci. [5] 41, 759 (1955).
2. I. B. Johns, E. A. McElhill, and J. O. Smith, J. Chem. and Eng. Data, 7, 277 (1962).
3. G. M. Brooke, J. Burdon, M. Stacey, and J. C. Tatlow, J. Chem. Soc., 1768 (1960).
4. L. A. Wall, W. J. Pummer, J. E. Fern, and J. M. Antonucci, J. Res. Natl. Bur. Stds., 67A, 481 (1963).
5. R. J. Harper, E. J. Soloski, and C. Tamborski, J. Org. Chem., 29, 2385 (1964).
6. D. G. Holland, G. J. Moore, and C. Tamborski, AFML-TR-64-367 Air Force Materials Laboratory, Wright-Patterson AFB, Ohio (1965).
7. E. S. Blake, G. A. Richardson, and J. A. Webster, RTD-TDR-63-4186 Research and Technology Division, Wright-Patterson AFB, Ohio (1963).
8. J. Burdon, J. Castaner, and J. C. Tatlow, J. Chem. Soc., 5017 (1964).
9. G. Baum and F. Short, AFML-TR-65-347 Air Force Materials Laboratory, Wright-Patterson AFB, Ohio (1965).
10. E. S. Blake, W. C. Hammann, J. W. Edwards, et al., J. Chem. and Eng. Data, 6, 87 (1961).



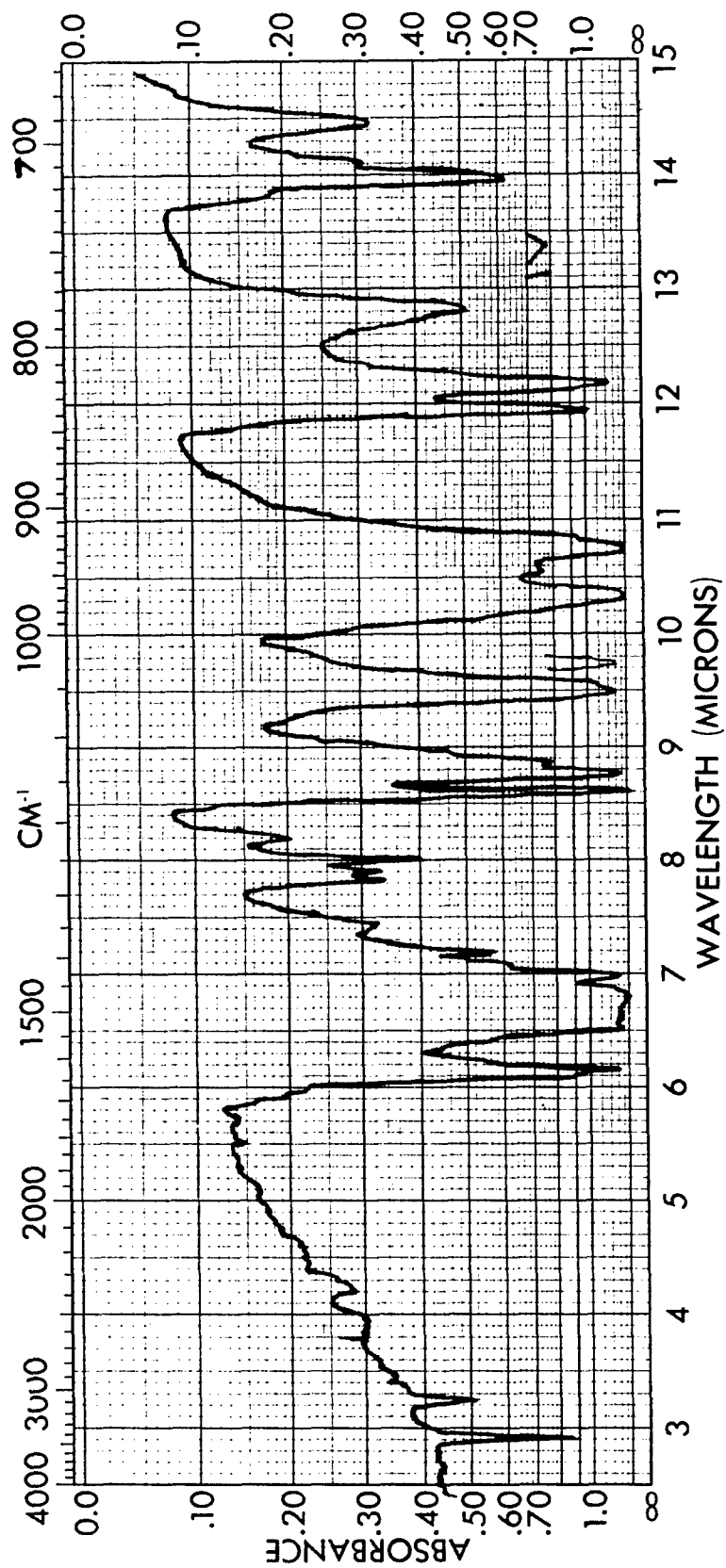
Compound No. I. Decafluorodiphenylamine



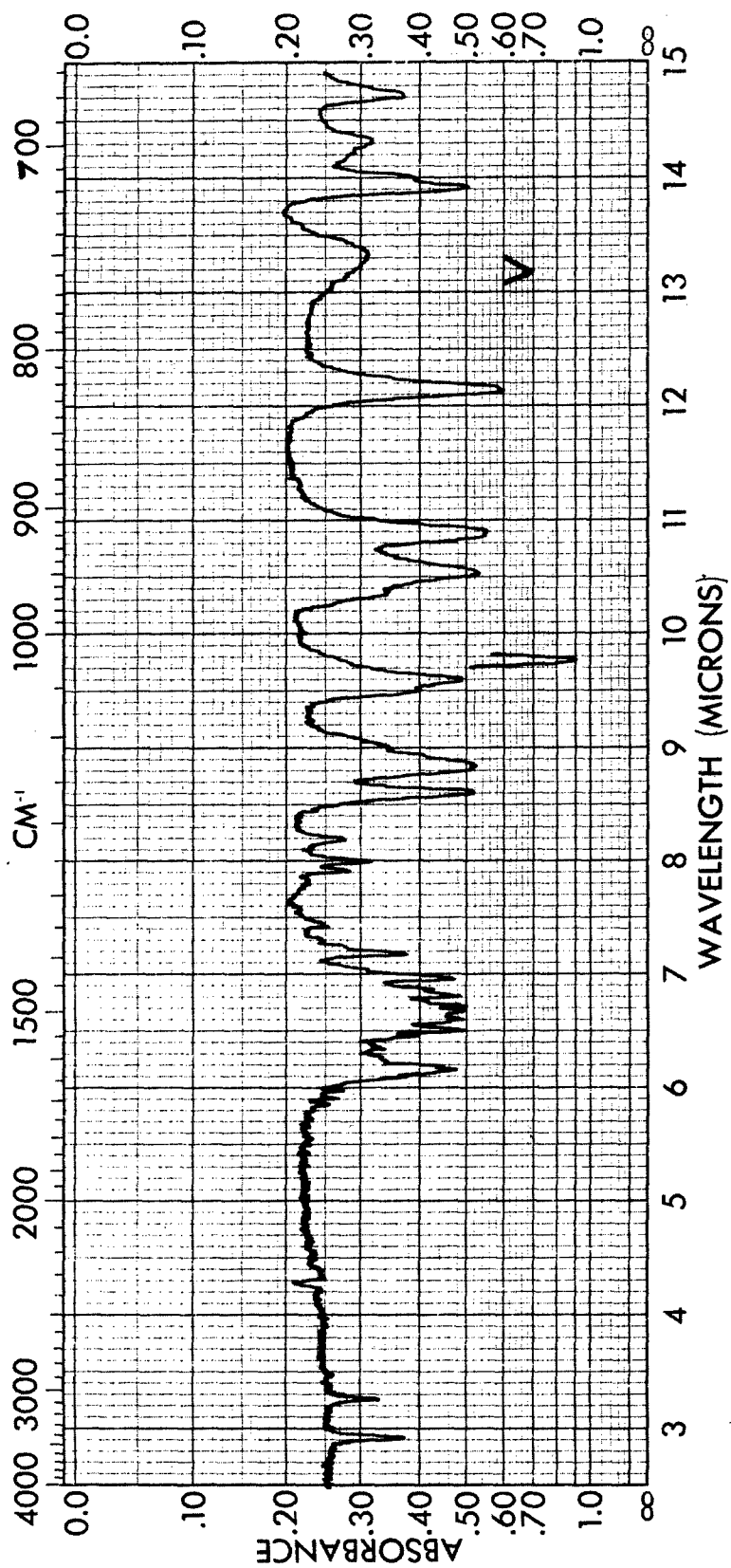
Compound No. II. 4H-Nonafluorodiphenylamine



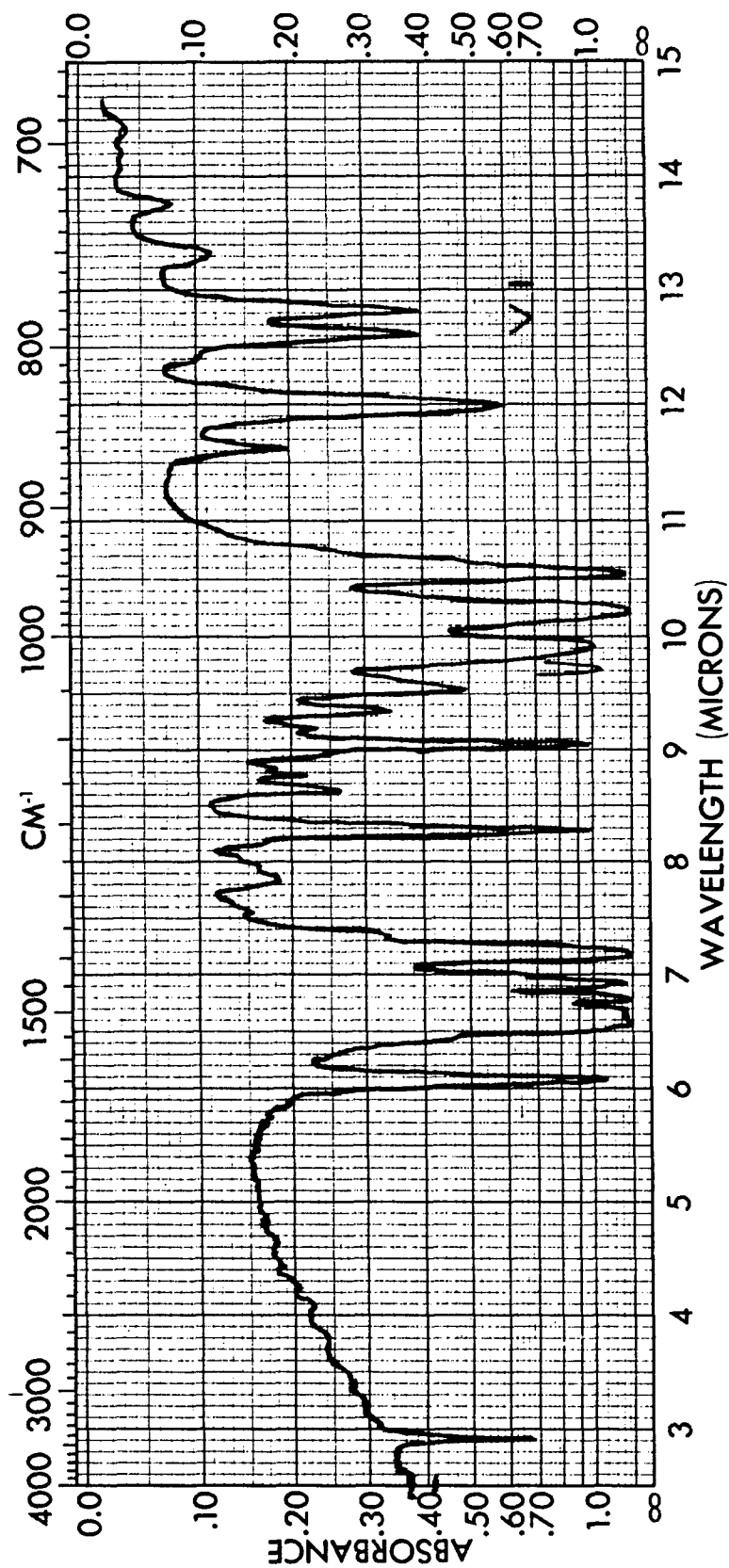
Compound No. III. 4-Bromo-nonafluorodiphenylamine



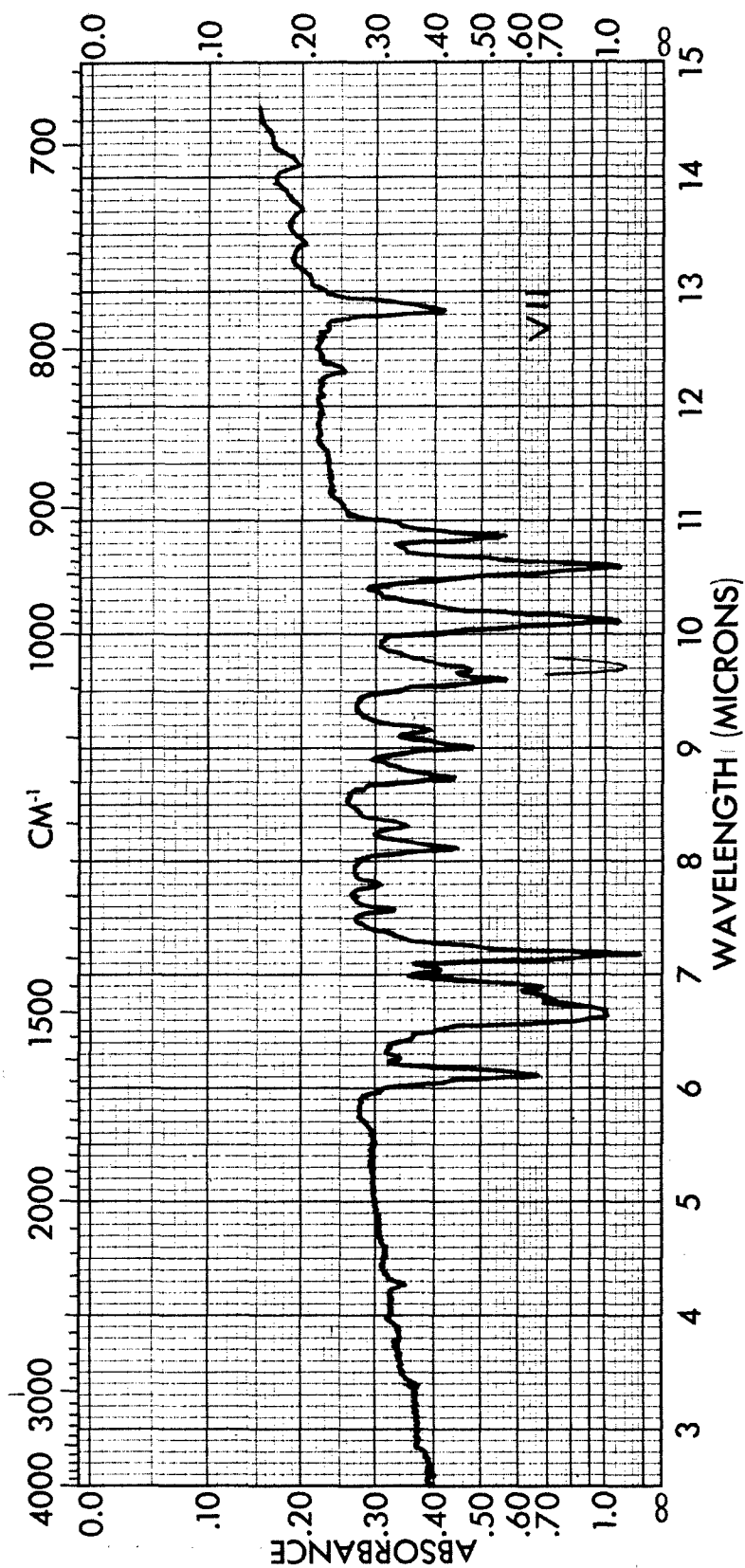
Compound No. IV. 4H,4'-Bromo-octafluorodiphenylamine



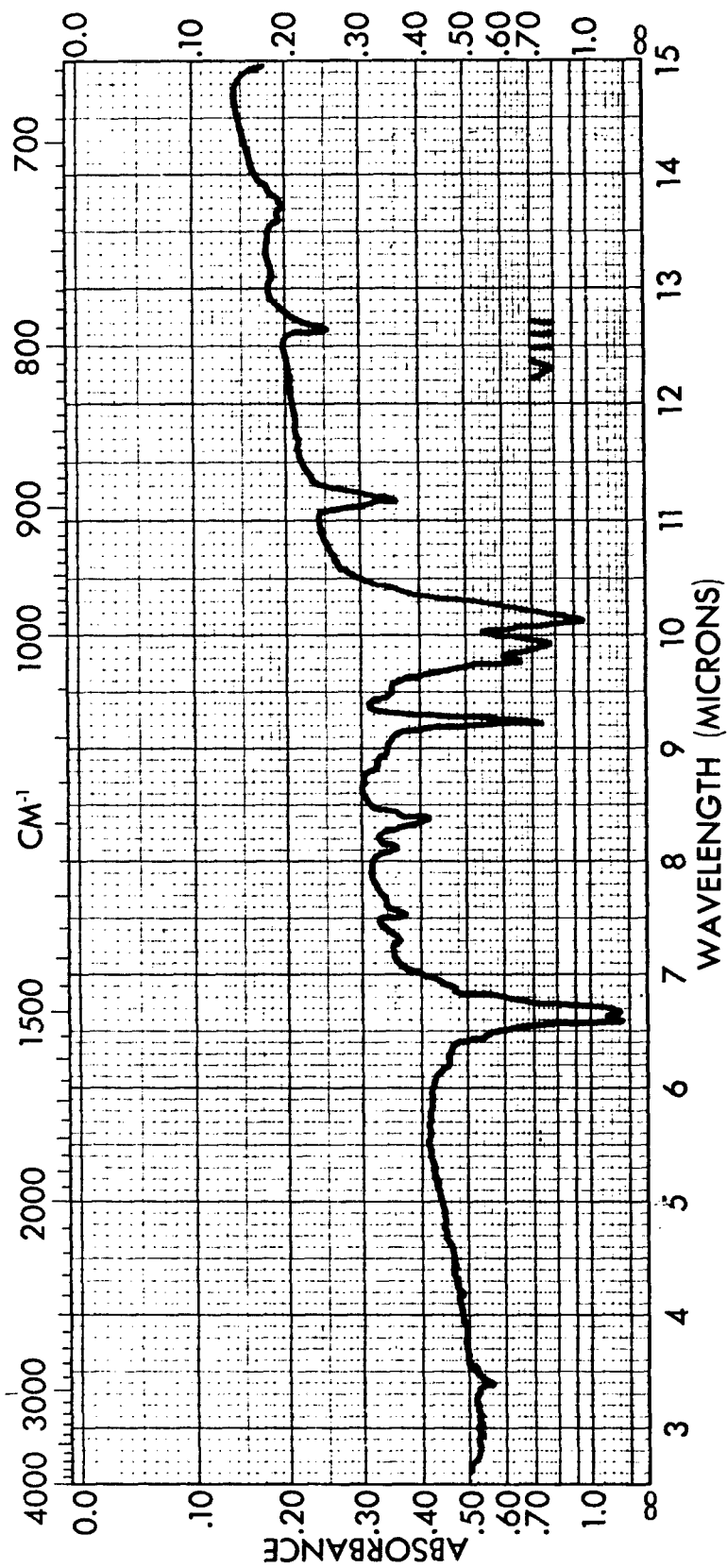
Compound No. V. Di(4H-tetrafluorophenyl)amine



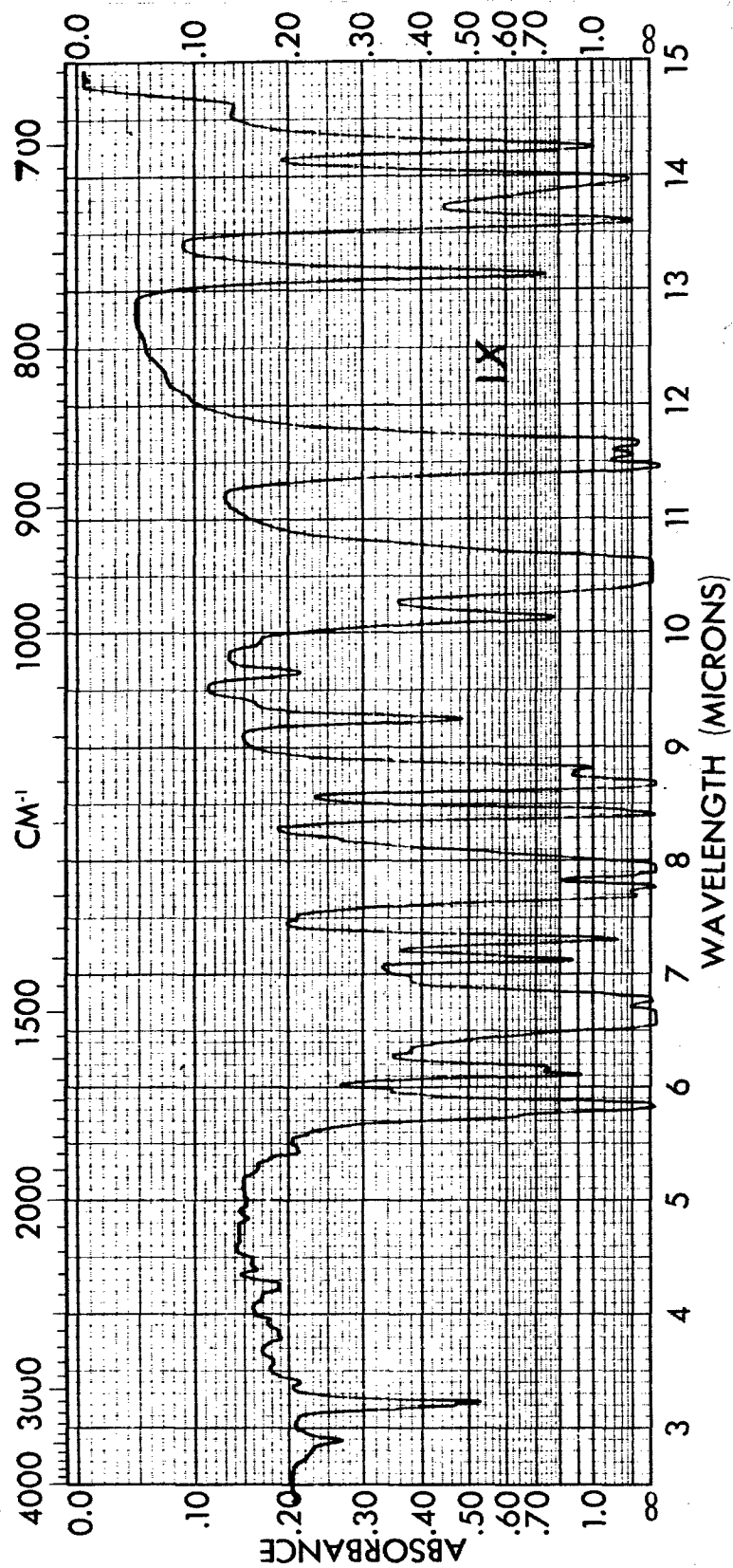
Compound No. VI. N-Pentafluorophenyl-2-heptafluoronaphthylamine



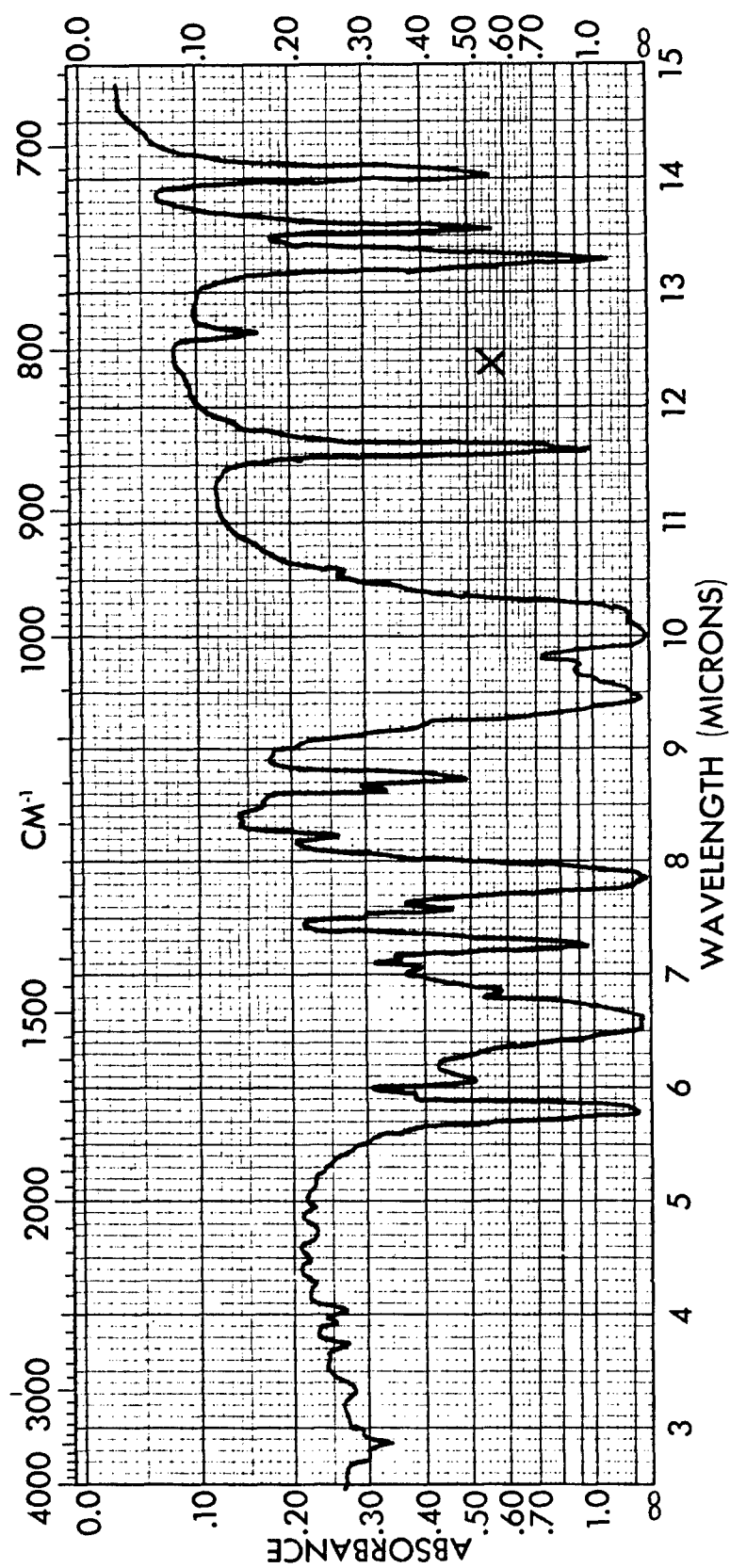
Compound No. VII. N-Methyl-N-pentafluorophenyl-2-heptafluoronaphthylamine



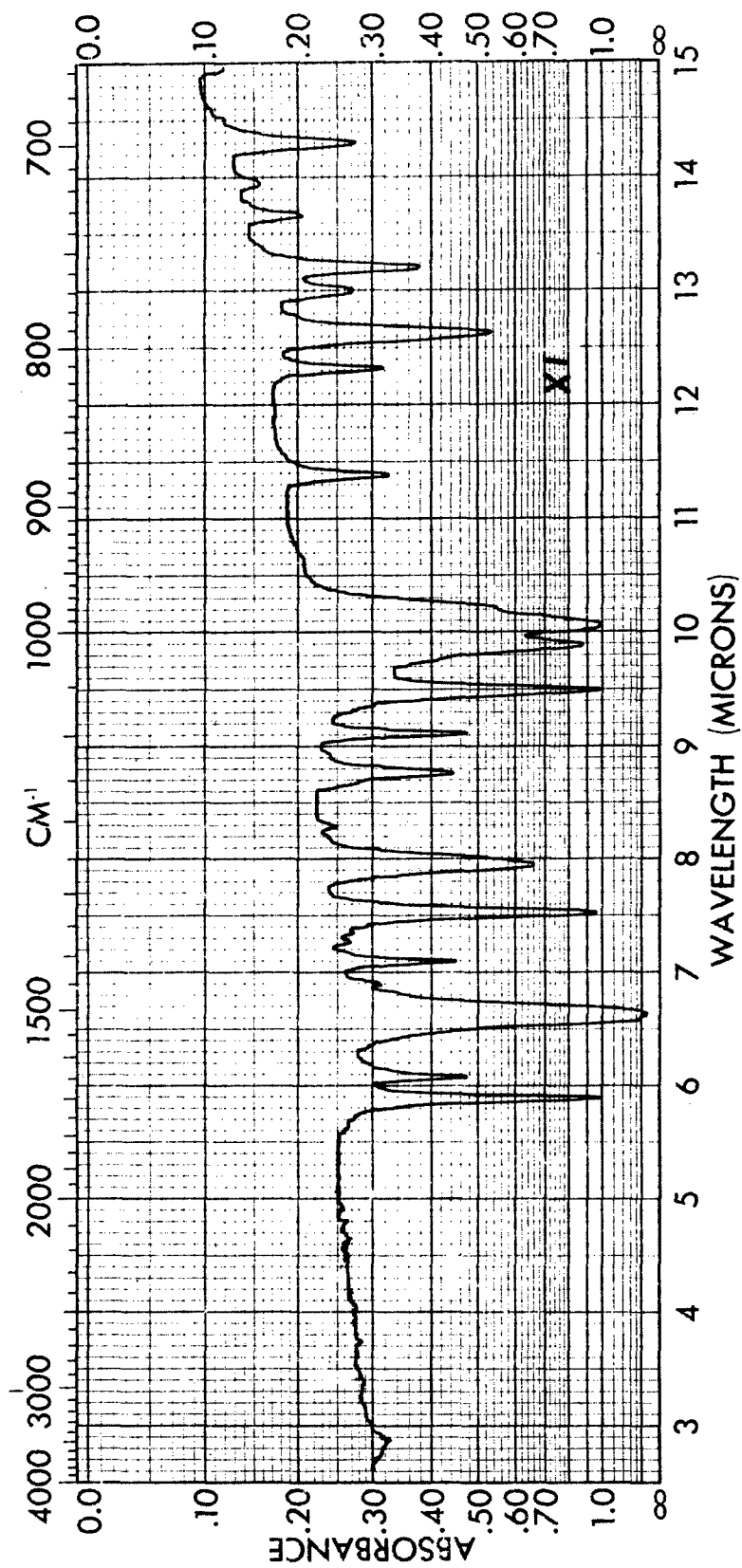
Compound No. VIII, N-Methyldecafluorodiphenylamine



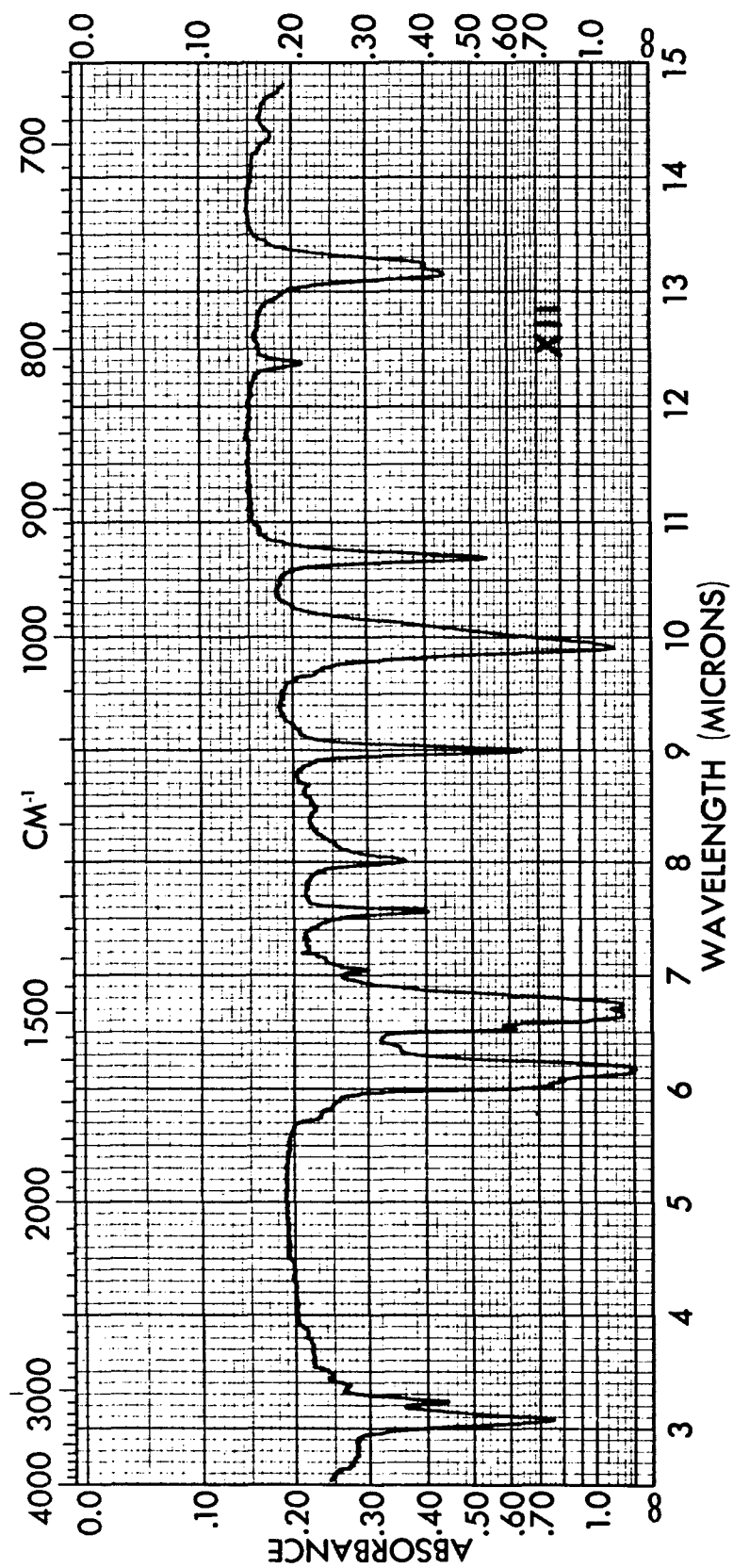
Compound No. IX. Di(4-H-tetrafluorophenyl)acetamide



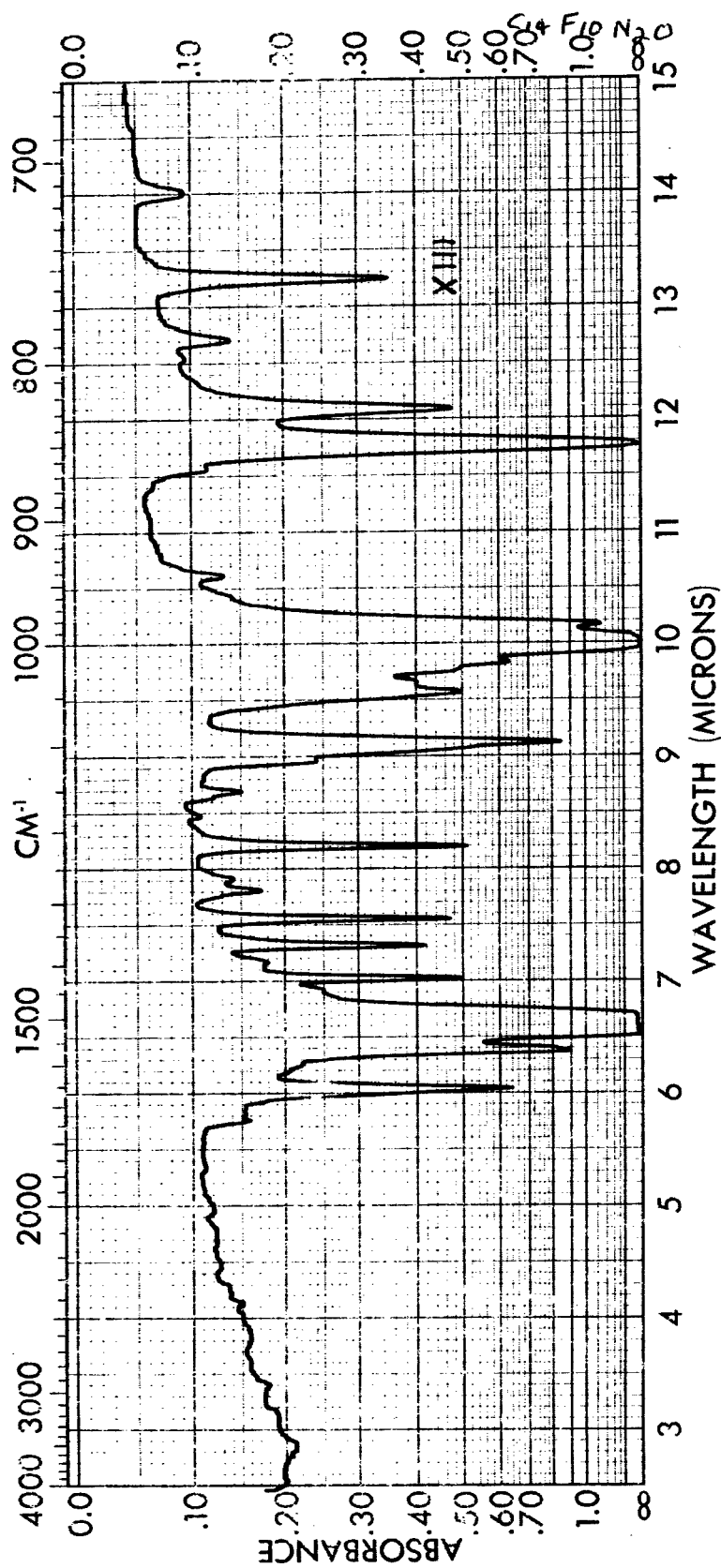
Compound No. X. Decafluorodiphenylacetamide



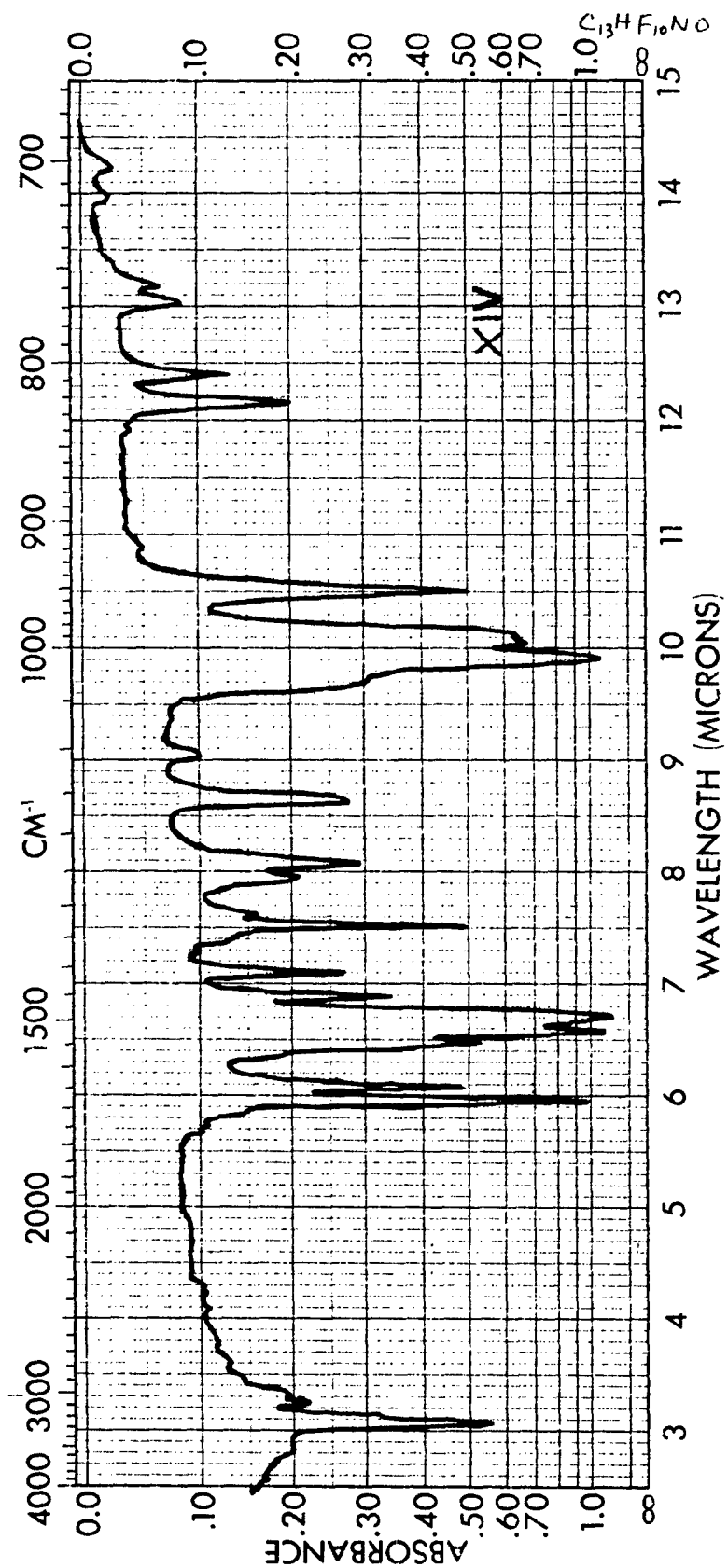
Compound No. XI. Pentadecafluorodiphenylbenzamide



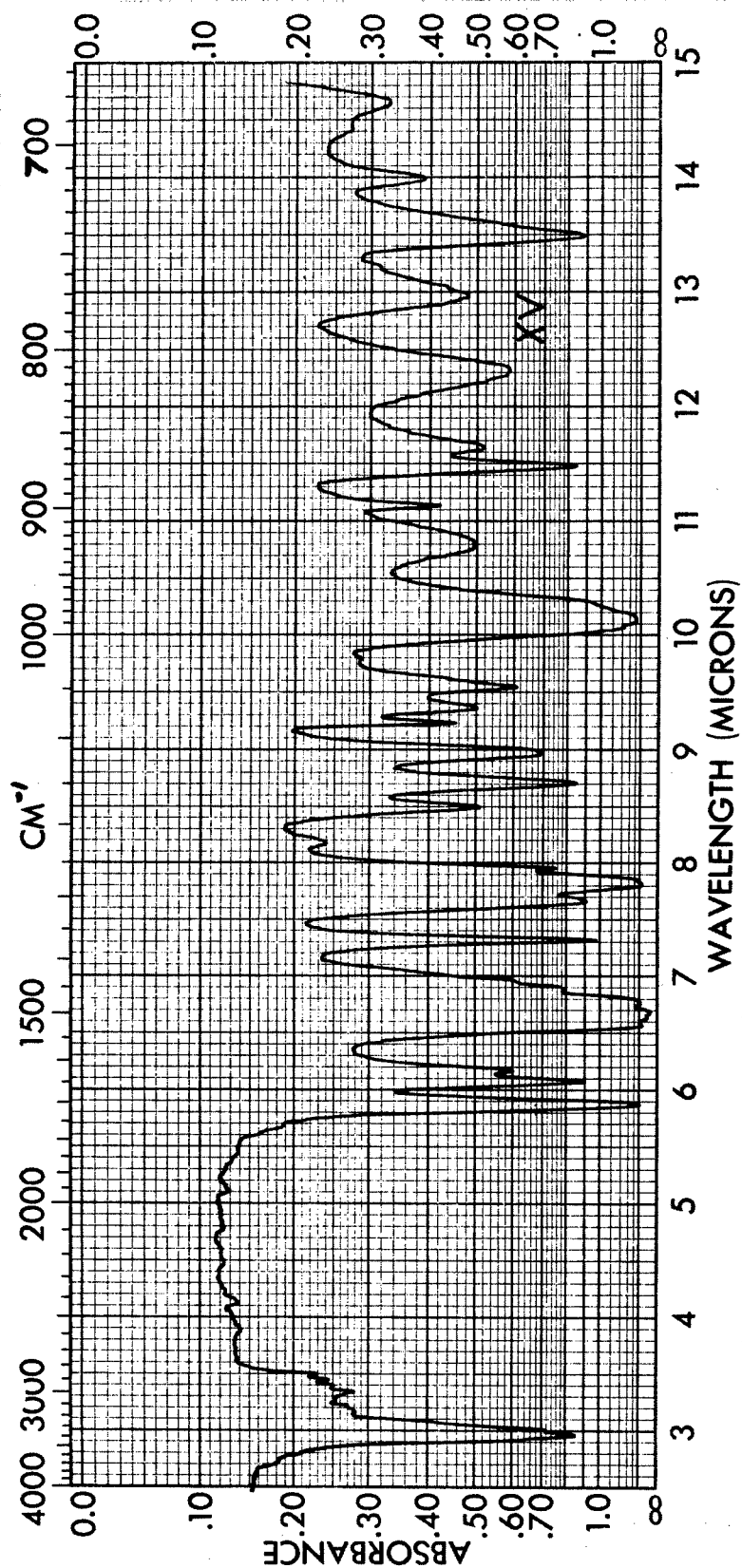
Compound No. XII. 1,2-Di(pentafluorobenzoyl)hydrazine



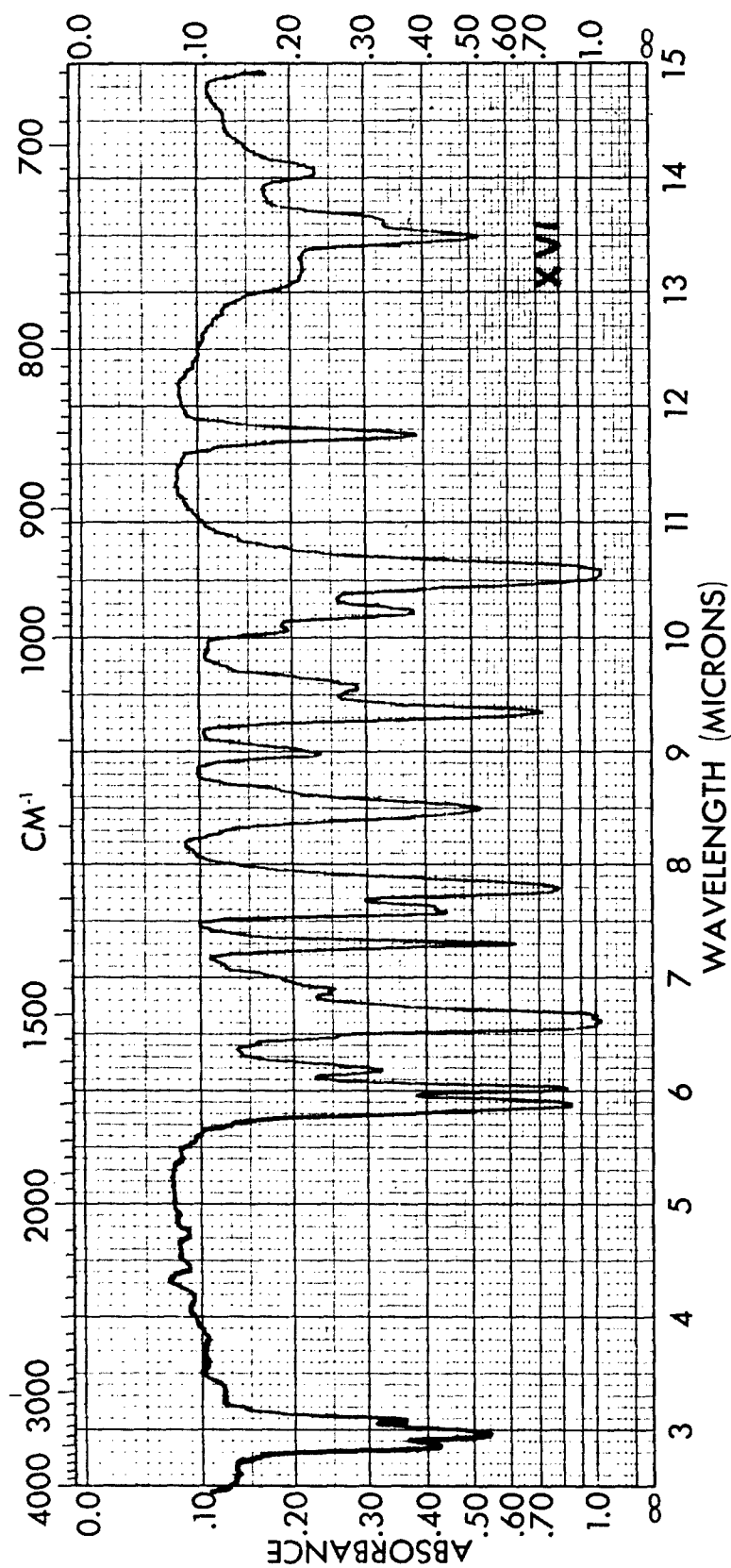
Compound No. XIII. 2,5-Di(pentafluorophenyl)-1,3,4-oxadiazole



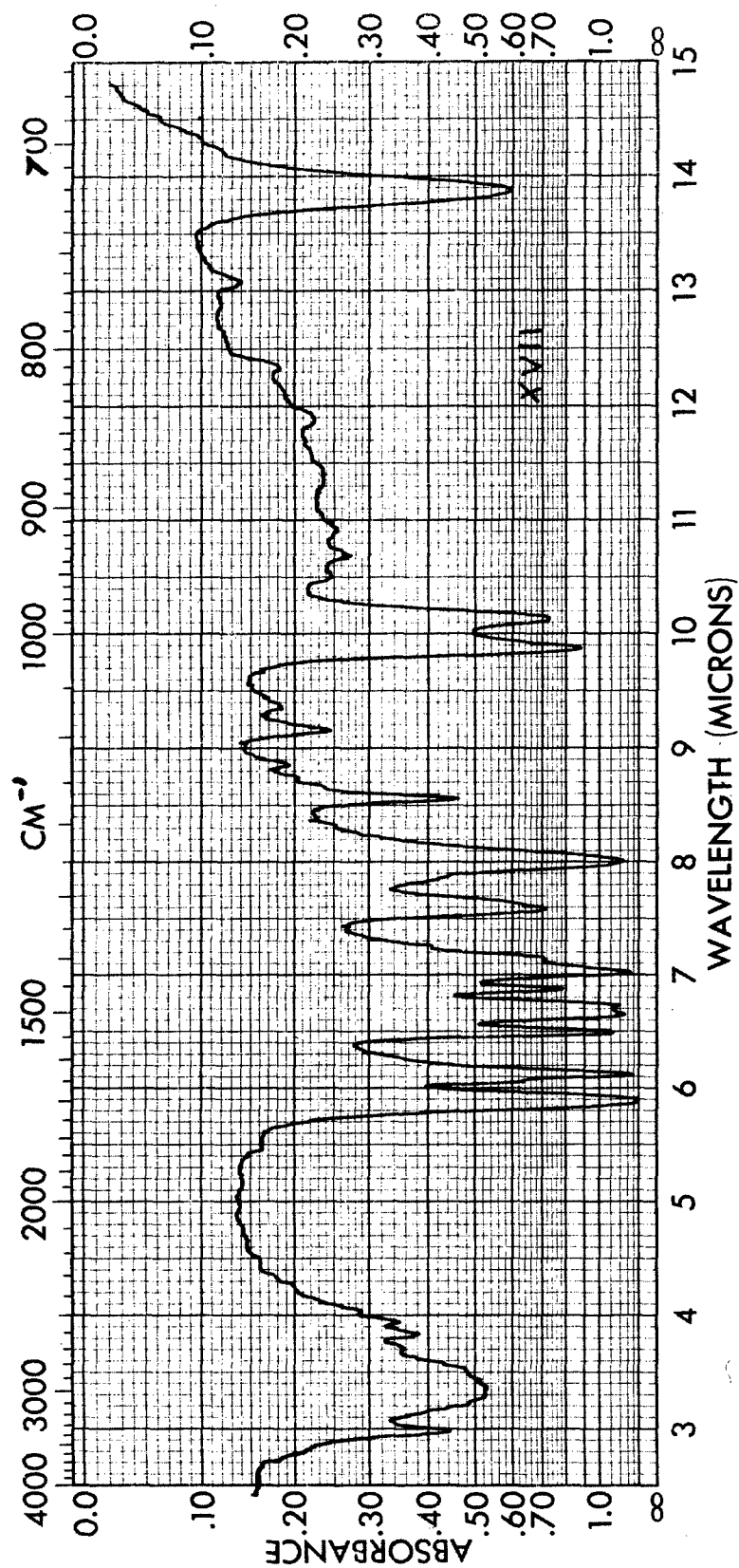
Compound No. XIV. Decafluorobenzanilide



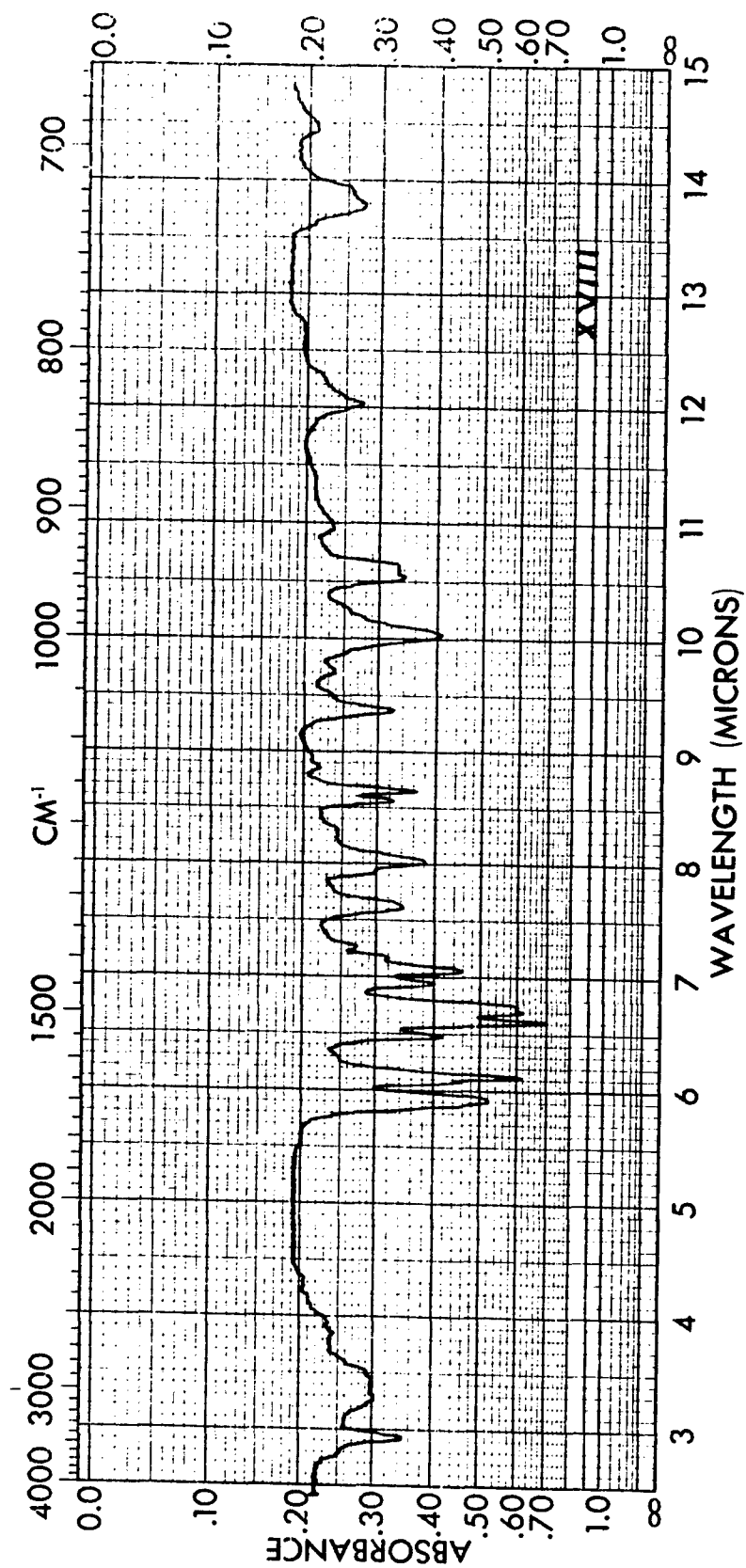
Compound No. XV. Di(4-hydrazinotetrafluorophenyl)acetamide



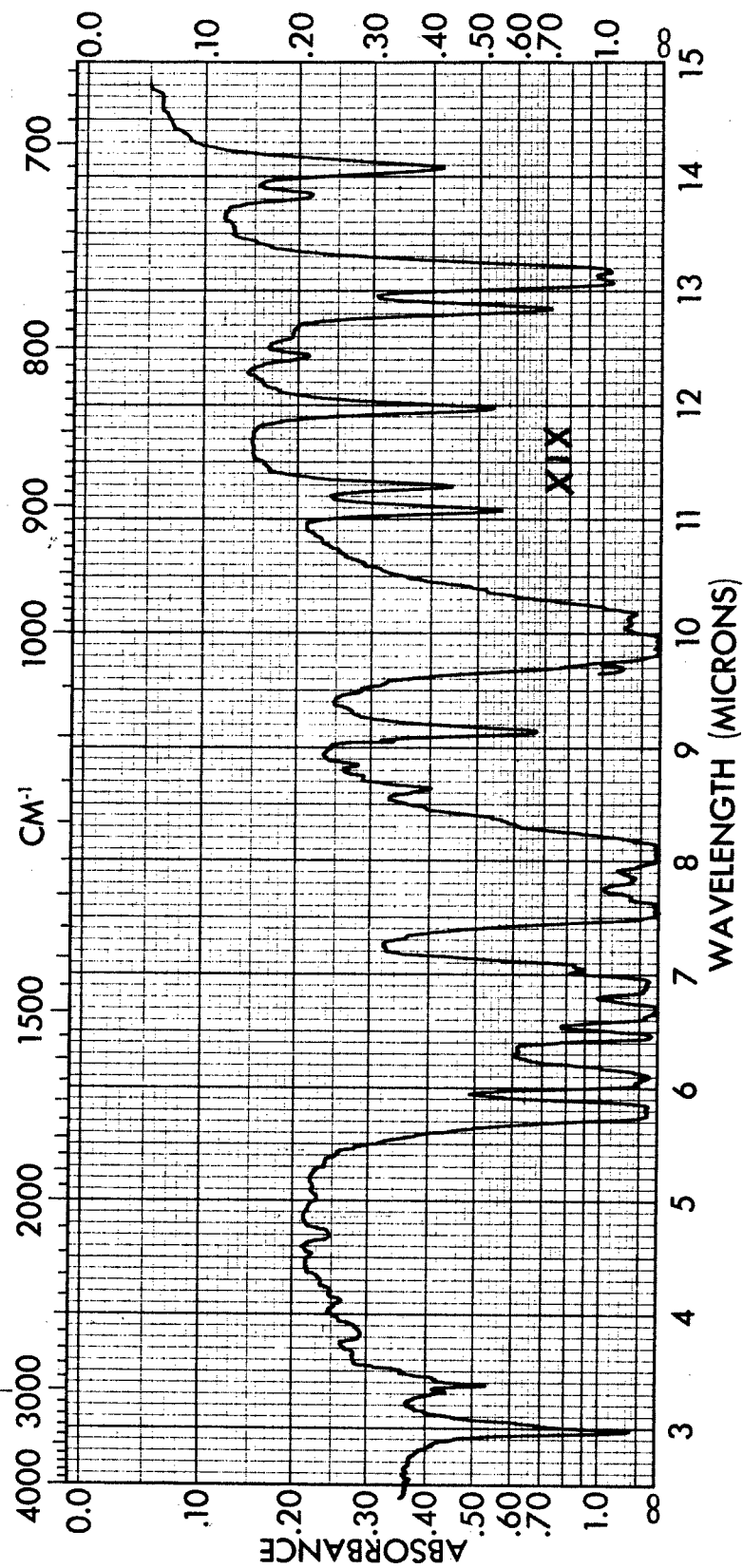
Compound No. XVI. Di(4-aminotetrafluorophenyl)acetamide



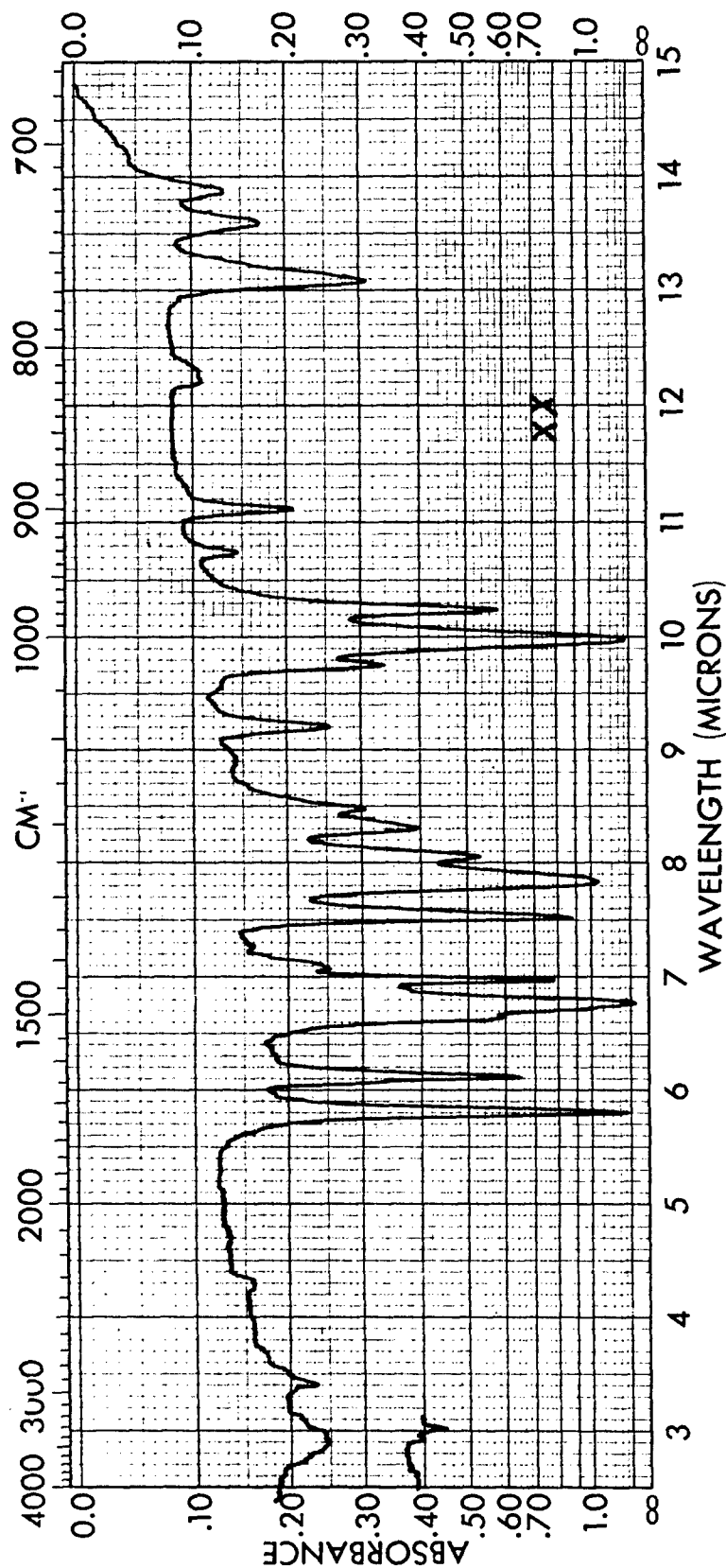
Compound No. XVII. Di(4-carboxytetrafluorophenyl)amine



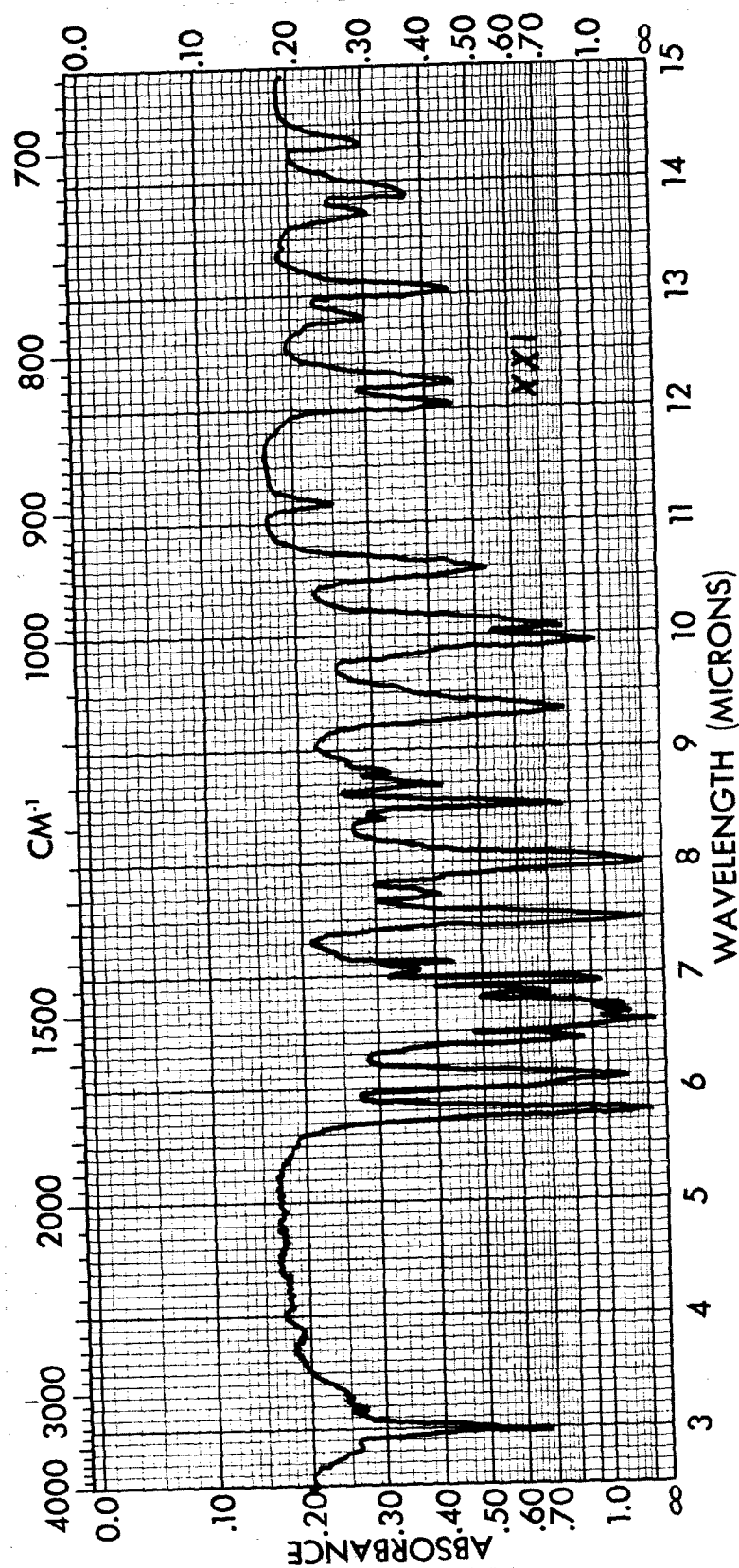
Compound No. XVIII. 4H,4'-Carboxyoctafluorodiphenylamine



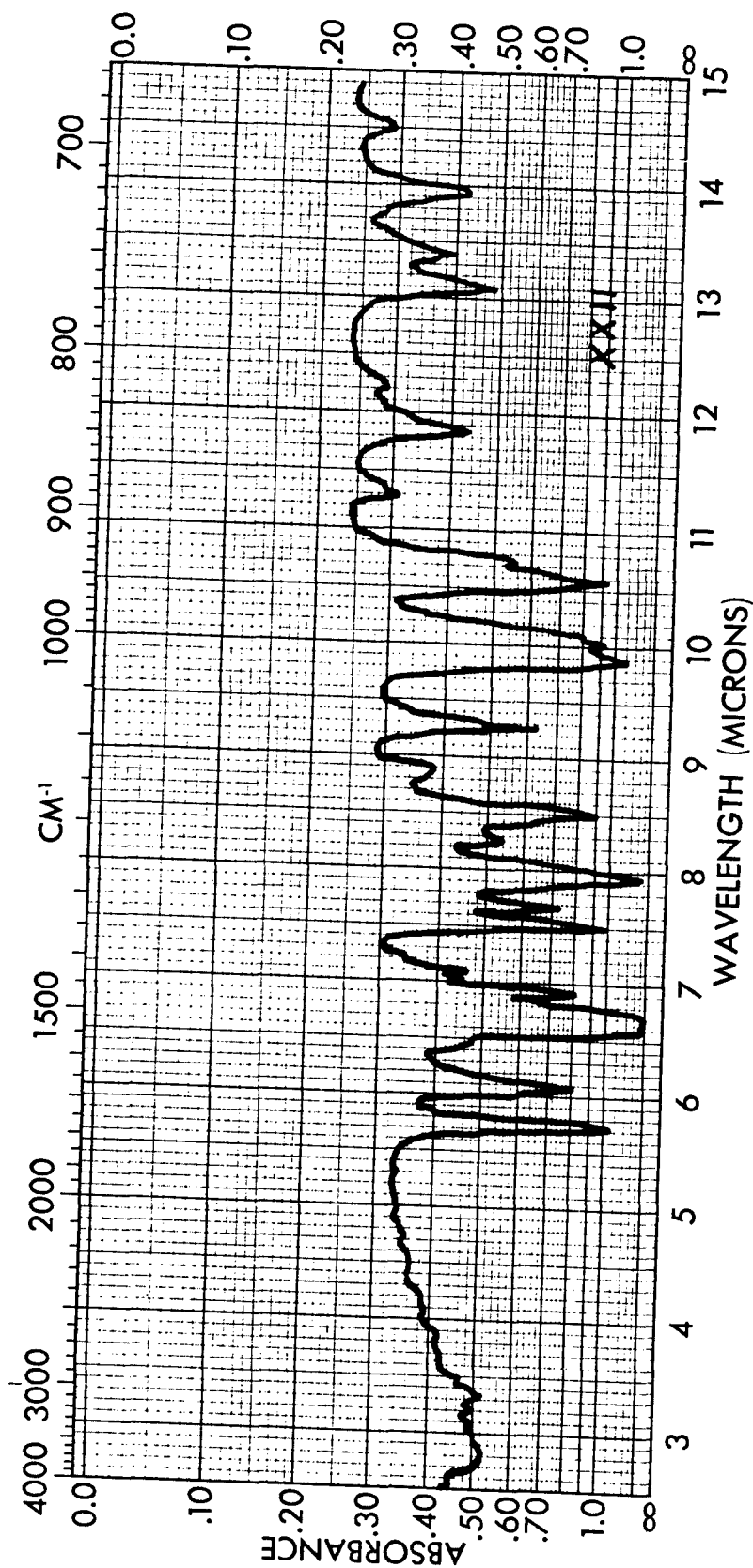
Compound No. XIX. Di(4-carbomethoxytetrafluorophenyl)amine



Compound No. XX. N-Methyl-di(4-carbomethoxytetrafluorophenyl)amine



Compound No. XXI. 4H,4'-Carbomethoxyoctafluorodiphenylamine



Compound No. XXII. N-Methyl-4H,4'-carbomethoxyoctafluorodiphenylamine

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author) Nonmetallic Materials Division Air Force Materials Laboratory Research and Technology Division		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP
3. REPORT TITLE FLUOROAROMATIC CHEMISTRY: Synthesis of Nitrogen Containing Fluoroaromatic Compounds		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Summary Report (January 1963 to January 1965)		
5. AUTHOR(S) (Last name, first name, initial) Baum, George Tamborski, Christ		
6. REPORT DATE October 1966	7a. TOTAL NO. OF PAGES 43	7b. NO. OF REFS 10
8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S) AFML-TR-66-211	
b. PROJECT NO. 7340		
c. Task No. 734004	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.		
10. AVAILABILITY/LIMITATION NOTICES This document may be further distributed by any holder <u>only</u> with specific prior approval of the Polymer Branch (MANP), Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio 45433.		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Air Force Systems Command United States Air Force Wright-Patterson AFB, Ohio	
13. ABSTRACT The present research was undertaken as part of a broad program to investigate the potential utility of polyfluoroaromatic compounds as thermally or oxidatively resistant non-metallic materials. Nucleophilic substitution reactions of polyfluoroanilines with fluoroaromatics led to a variety of polyfluorodiphenylamines which are structurally related to known antioxidants. These amines were further converted into diamines and diacids. Several model compounds were prepared for thermal stability studies. Amides of secondary polyfluoroamines appear to possess a high degree of stability.		

DD FORM 1 JAN 64 1473

UNCLASSIFIED

Security Classification

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Polyfluoroaromatics Compounds Antioxidants Polymer Intermediates Thermal Stability						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.

UNCLASSIFIED

Security Classification